Supplementary Information for

Divergent syntheses of iodinated isobenzofuranones and isochromenones by iodolactonization of 2-alkynylbenzoic acids in ionic liquids

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Preparation of Substrates and Characterization Data

2-Alkynylbenzoic acids **1** were prepared by Sonogashira coupling between the corresponding methyl 2-halobenzoates and terminal alkynes followed by hydrolysis,[1] as described below.

Preparation of methyl 2-halobenzoates. Methyl 2-iodobenzoate was commercially available. Methyl 2-bromo-5-chlorobenzoate and methyl 3-methyl-2-iodobenzoate were prepared by Fischer esterification, according to the following procedure: To a stirred solution of the 2-halobenzoic acid [10.0 mmol; 2-bromo-5-chlorobenzoic acid (commercially available), 2.35 g; 3-methyl-2-iodobenzoic acid,[2] 2.62 g] in MeOH (4.1 mL) was added, dropwise, concentrated H_2SO_4 (0.8 mL). The resulting mixture was allowed to reflux under stirring for 4 h. After cooling, water (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (10 × 3 mL). The combined organic layers were washed with saturated $NaHCO_3$ to neutral pH and then dried over Na_2SO_4. After evaporation of the solvent, the crude methyl esters were sufficiently pure to be used as such for the next step without further purification.

Methyl 2-bromo-5-chlorobenzoate. Yield: 2.35 g, starting from 2.35 g of 5-chloro-2-iodobenzoic acid (94 %). Colorless solid, mp = 37-38 °C (lit.,[3] 37-38 °C). IR (KBr): ν = 1734 (s), 1461 (w), 1434 (w), 1295 (m), 1251 (m), 1119 (m), 1101 (m), 1034 (m), 962 (w), 814 (m), 779 (w), 753 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (distorted dd, J = 2.6, 0.8, 1 H), 7.58 (distorted dd, J = 8.5, 0.8, 1 H), 7.30 (distorted ddd, J = 8.5, 2.6, 0.8, 1 H), 3.94 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 135.5, 133.4, 133.3, 132.6, 131.3, 119.7, 52.7; GC-MS: m/z = 250 (60) [$(M+2)^+$], 248 (50) (M^+), 219 (100), 217 (89), 191 (24), 189 (23), 110 (18), 75 (24); anal.

calcd for $C_8H_6BrClO_2$ (249.49): C, 38.51; H, 2.42; Br, 32.03; Cl, 14.21; found C, 38.54; H, 2.40; Br, 32.00; Cl, 14.24. The spectroscopic data were in good agreement with those reported.[4]

Methyl 3-methyl-2-iodobenzoate. Yield: 2.35 g, starting from 2.62 g of 3-methyl-2-iodobenzoic acid (85 %). Yellow oil. IR (KBr): ν = 1733 (s), 1572 (w), 1433 (m), 1399 (w), 1294 (m), 1265 (w), 1242 (w), 1194 (m), 1177 (w), 1143 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.18 (m, 3 H), 3.91 (s, 3 H), 2.47 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6, 143.2, 138.3, 131.7, 127.7, 127.0, 99.9, 52.5, 29.6; GC-MS m/z = 276 (89) [M^+], 245 (100), 217 (17), 149 (14), 134 (3), 119 (8), 90 (53); anal. calcd for $C_9H_9IO_2$ (276.07): C, 39.16; H, 3.29; I, 45.97; found C, 39.15; H, 3.30; I, 45.99. The spectroscopic data agreed with those reported.[5]

Sonogashira coupling between methyl 2-halobenzoates and terminal alkynes to give methyl 2-alkynyl benzoates. The method of Kundu[6] was adapted. A solution of the methyl 2-halobenzoate derivative (4.0 mmol; methyl 2-iodobenzoate, 1.05 g; methyl 2-bromo-5-chlorobenzoate, 1.10 g; methyl 2-iodo-3-methylbenzoate, 1.10 g), $PdCl_2(PPh_3)_2$ (99.2 mg, 0.14 mmol), CuI (61.0 mg, 0.32 mmol) and Et_3N (1.9 mL) in anhydrous DMF (10 mL) was allowed to stir under nitrogen for 1 h. The terminal alkyne (3,3-dimethyl-1-butyne, 395 g; 1-hexyne, 395 mg; phenylacetylene, 490 mg; 3-ethynylthiophene, 520 mg; 1-ethynyl-4-methylbenzene, 558 mg; 1-ethynylcyclohexene, 510 mg; trimethylsilylacetylene, 470 mg) (4.8 mmol) was then added under nitrogen, and the resulting mixture was heated at 80-85 °C (oil bath) for 15 h. After cooling, CH_2Cl_2 (100 mL) was added, and the mixture washed with water (3 × 100 mL). After drying over Na_2SO_4, the solvent was evaporated, and the residue purified by column chromatography on silica gel using hexane-AcOEt from 99:1 to 95:5 as eluent.

Methyl 2-(3,3-dimethylbut-1-ynyl)benzoate. Yield: 720 mg, starting from 1.05 g of methyl 2-iodobenzoate (83 %). Yellow oil. IR (film): ν = 2239 (w), 1720 (s), 1597 (w), 1447 (w), 1290 (m), 1250 (m), 1128 (m), 1081 (m), 757 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.91-7.83 (m, 1 H), 7.52-7.45 (m, 1 H), 7.22 (td, J = 7.6, 1.5, 1 H), 7.29 (td, J = 7.6, 1.5, 1 H), 3.91 (s, 3 H), 1.34 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 167.3, 133.9, 132.2, 131.4, 130.2, 127.1, 124.2, 103.6, 77.9, 51.9, 30.9, 28.2; GC-MS: m/z = 216 (39) [M$^+$], 201 (100), 185 (14), 157 (87), 141 (42), 115 (55); anal. calcd for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46; found C, 77.73; H, 7.49.

Methyl 5-chloro-2-(3,3-dimethylbut-1-ynyl)benzoate. Yield: 800 mg, starting from 1.10 g of methyl 2-bromo-5-chlorobenzoate (80 %). Yellow oil. IR (film): ν = 2239 (w), 1720 (s), 1473 (m), 1435 (m), 1287 (s), 1239 (s), 1142 (w), 1077 (w), 974 (w), 829 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.85 (d, J = 2.2, 1 H), 7.40 (distorted d, J = 8.4, 1 H), 7.35 (distorted dd, J = 8.4, 2.2, 1 H), 3.91 (s, 3 H), 1.34 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 165.9, 135.1, 133.5, 133.0, 131.5, 130.2, 122.8, 104.7, 77.0, 52.1, 30.8, 28.3; GC-MS: m/z = 252 (11) [(M+2)$^+$], 250 (33) [M$^+$], 237 (33), 235 (100), 215 (47), 203 (41), 191 (30), 156 (71), 149 (14), 139 (21), 128 (14), 115 (17); anal. calcd for $C_{14}H_{15}ClO_2$ (250.72): C, 67.07; H, 6.03; Cl, 14.14; found C, 67.09; H, 6.06; Cl, 14.11.

Methyl 2-(hex-1-ynyl)benzoate. Yield: 695 mg, starting from 1.05 g of methyl 2-iodobenzoate (80 %). Yellow oil. IR (film): ν = 2229 (m), 1733 (s), 1597 (w), 1567 (w), 1485 (m), 1433 (m), 1294 (m), 1251 (m), 1128 (m), 1083 (m), 964 (w), 758 (m), 702 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.87 (dd, J = 7.6, 1.2, 1 H), 7.50 (distorted d, J = 7.6, 1 H), 7.40 (td, J = 7.6, 1.2, 1 H), 7.29 (td, J = 7.6, 1.2, 1 H), 3.91 (s, 3 H), 2.48 (t, J = 7.0, 2 H), 1.69-1.43 (m, 4 H), 0.95 (t, J = 7.2, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 167.0, 134.2, 132.0, 131.5, 130.1, 127.1, 124.5, 96.0, 79.2, 52.0, 30.8, 22.0, 19.5, 13.7; GC-MS: m/z = 216 (14) [M$^+$], 201 (20), 183 (12), 174

(100), 159 (44), 143 (23), 131 (27), 115 (36); anal. calcd for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46; found C, 77.76; H, 7.48. The spectroscopic data agreed with those reported.[7]

Methyl 2-(2-phenylethynyl)benzoate. Yield: 830 mg, starting from 1.05 g of methyl 2-iodobenzoate (88 %). Yellow oil. IR (film): ν = 2218 (w), 1730 (s), 1599 (w), 1568 (w), 1494 (m), 1433 (w), 1293 (m), 1252 (m), 1128 (m), 1078 (m), 964 (w), 756 (m), 690 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98-7.93 (m, 1 H), 7.65-7.55 (m, 3 H), 7.45 (td, J = 7.6, 1.4, 1 H), 7.38-7.30 (m, 4 H), 3.94 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 134.0, 131.9, 131.73, 131.68, 130.5, 128.5, 128.4, 127.9, 123.7, 123.3, 94.4, 88.3, 52.2; GC-MS: m/z = 236 (100) [M^+], 221 (76), 205 (24), 193 (36), 176 (41), 165 (38), 151 (17), 126 (4), 102 (10); anal. calcd for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12; found C, 81.32; H, 5.15. The spectroscopic data agreed with those reported.[7,8]

Methyl 5-chloro-2-(2-phenylethynyl)benzoate. Yield: 848 mg, starting from 1.10 g of methyl 2-bromo-5-chlorobenzoate (78 %). Yellow solid, mp = 53-54 °C. IR (KBr): ν = 2216 (w), 1734 (s), 1493 (m), 1435 (w), 1289 (s), 1242 (s), 1109 (m), 1073 (m), 827 (w), 755 (m), 689 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J = 2.3, 1 H), 7.60-7.49 (m, 2 H), 7.42 (distorted dd, J = 8.4, 2.2, 1 H), 7.38-7.29 (m, 4 H), 3.95 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 135.1, 133.8, 133.1, 131.8, 131.7, 130.6, 128.7, 128.4, 95.4, 87.3, 52.4; GC-MS m/z = 270 (100) [M^+], 255 (73), 239 (18), 227 (34), 199 (25), 176 (53), 150 (13), 119 (8), 88 (30); anal. calcd for $C_{16}H_{11}ClO_2$ (270.71): C, 70.99; H, 4.10; Cl, 13.10; found C, 70.97; H, 4.13; Cl, 13.11.

Methyl 2-[2-(thiophen-3-yl)ethynyl]benzoate. Yield: 795 mg, starting from 1.05 g of methyl 2-iodobenzoate (82 %). Yellow solid, mp = 36-38 °C. IR (KBr): ν = 2216 (w), 1728 (s), 1595 (w), 1566 (w), 1481 (w), 1432 (w), 1292 (m), 1282 (m), 1253 (m), 1126 (m), 1076 (m), 940 (w), 870 (w), 783 (m), 756 (m), 698 (m), 625 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, *J* = 7.6, 1.4, 1 H), 7.62 (distorted dd, *J* = 7.6, 1.3, 1 H), 7.59-7.54 (m, 1 H), 7.46 (td, *J* = 7.6, 1.4, 1 H), 7.34 (distorted td, *J* = 7.6, 1.3, 1 H), 7.29 (distorted dd, *J* = 5.0, 2.9, 1 H), 7.23 (distorted dd, *J* = 5.0, 1.1, 1 H), 3.94 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 133.9, 131.7, 130.5, 129.9, 129.1, 127.8, 125.4, 123.7, 122.4, 89.6, 87.8, 52.1; GC-MS *m/z* = 242 (100) [M^+], 227 (65), 211 (21), 199 (57), 183 (12), 171 (26), 139 (54), 105 (12), 91 (24); anal. calcd for $C_{14}H_{10}O_2S$ (242.29): C, 69.40; H, 4.16; S, 13.21; found C, 69.38; H, 4.13; S, 13.24. The spectroscopic data agreed with those reported.[9]

Methyl 3-methyl-2-(2-phenylethynyl)benzoate. Yield: 760 mg, starting from 1.10 g of methyl 2-iodo-3-methylbenzoate (76 %). Yellow oil. IR (film): ν = 2213 (w), 1730 (s), 1597 (w), 1491 (m), 1436 (m), 1291 (m), 1268 (m), 1193 (m), 1137 (m), 1017 (m), 876 (w), 756 (s), 691 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79-7.73 (m, 1 H), 7.61-7.35 (m, 2 H), 7.40-7.30 (m, 4 H), 7.23 (t, *J* = 7.7, 1 H), 3.93 (s, 3 H), 2.55 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 141.8, 132.9, 132.5, 131.6, 128.5, 128.4, 127.7, 127.4, 123.5, 123.0, 99.3, 86.6, 52.1, 21.3; GC-MS *m/z* = 250 (77) [M^+], 235 (100), 219 (29), 207 (47), 191 (45), 189 (72), 179 (46), 178 (26), 165 (19), 95 (27); anal. calcd for $C_{17}H_{14}O_2$ (250.29): C, 81.58; H, 5.64; found C, 81.56; H, 5.65.

Methyl 2-(2-p-tolylethynyl)benzoate. Yield: 842 mg, starting from 1.05 g of methyl 2-iodobenzoate (84 %). Yellow oil. IR (film): ν = 2216 (m), 1731 (s), 1595 (w), 1566 (w), 1510 (m), 1433 (m), 1293 (m), 1252 (m), 1189 (w), 1127 (m), 1078 (m), 1040 (w), 965 (w), 818 (m), 757 (m), 700 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98-7.91 (m, 1 H), 7.65-7.58 (m, 1 H), 7.51-7.40 (m, 3 H), 7.37-7.28 (m, 1 H), 7.14 (distorted d, *J* = 7.9, 2 H), 3.94 (s, 3 H), 2.34 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 138.7, 133.9, 131.8, 131.6, 130.4, 129.1, 127.7, 123.9, 120.2, 94.6, 87.7, 52.1, 21.5; GC-MS *m/z* = 250 (100) [M^+], 235 (91), 219 (20), 207 (56), 189 (39), 179 (36), 165 (9), 125 (6), 109 (12), 95 (21); anal. calcd for $C_{17}H_{14}O_2$ (250.29): C, 81.58; H, 5.64;

found C, 81.60; H, 5.63. The spectroscopic data were in good agreement with those reported.[10]

Methyl 2-(2-cyclohexenylethynyl)benzoate. Yield: 823 mg, starting from 1.05 g of methyl 2-iodobenzoate (86 %). Yellow oil, IR (film): v = 2201 (m), 1718 (s), 1595 (w), 1566 (w), 1483 (m), 1434 (m), 1290 (m), 1251 (m), 1129 (m), 1077 (m), 758 (m), 700 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95-7.88 (m, 1 H), 7.54-7.49 (m, 1 H), 7.42 (td, J = 7.5, 1.4, 1H), 7.30 (td, J = 7.7, 1.4, 1H), 6.30-6.24 (m, 1 H), 3.91 (s, 3 H), 2.32-2.10 (m, 4 H), 1.74-1.53 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 136.0, 133.8, 131.61, 131.57, 130.3, 127.3, 124.2, 121.0, 96.4, 85.8, 52.0, 29.1, 25.8, 22.3, 21.5; GC-MS m/z = 240 (100) [M^+], 225 (47), 207 (20), 197 (20), 179 (25), 165 (27), 159 (21), 147 (18), 133 (17), 115 (16); anal. calcd for $C_{16}H_{16}O_2$ (240.30): C, 79.97; H, 6.71; found C, 79.99; H, 6.68. The spectroscopic data agreed with those reported.[11]

Methyl 2-[2-(trimethylsilyl)ethynyl]benzoate. Yield: 820 mg, starting from 1.05 g of methyl 2-iodobenzoate (88 %). Yellow oil. IR (film): v = 2106 (w), 1729 (s), 1595 (w), 1568 (w), 1484 (w), 1434 (m), 1298 (m), 1258 (m), 1133 (m), 1080 (m), 963 (w), 830 (w), 759 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93-7.87 (m, 1 H), 7.61-7.54 (m, 1 H), 7.43 (td, J = 7.5, 1.6, 1 H), 7.35 (td, J = 7.6, 1.4, 1 H), 3.92 (s, 3 H), 0.28 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.0, 134.6, 132.7, 131.6, 130.4, 128.3, 123.3, 103.4, 99.8, 52.1, 0.09; GC-MS m/z = 232 (5) [M^+], 217 (34), 187 (100), 158 (9), 143 (9), 131 (5), 129 (5), 115 (6), 101 (7), 93 (6); anal. calcd for $C_{13}H_{16}O_2Si$ (232.35): C, 67.20; H, 6.94; Si, 12.09; found C, 67.23; H, 6.93; Si, 12.07. The spectroscopic data agreed with those reported.[12]

Hydrolysis of methyl 2-alkynylbenzoates to give 2-alkynylbenzoic Acids 1. The method of Kundu[6] was adapted. A stirred solution of the methyl 2-alkynylbenzoate [2.5 mmol; methyl 2-(3,3-dimethylbut-1-ynyl)benzoate, 541 mg; methyl 5-chloro-2-(3,3-dimethylbut-1-ynyl)benzoate, 627 mg; methyl 2-(hex-1-ynyl)benzoate, 541 mg; methyl 2-(2-phenylethynyl)benzoate, 591 mg; methyl 5-chloro-2-(2-phenylethynyl)benzoate, 677 mg; methyl 2-[2-(thiophen-3-yl)ethynyl]benzoate, 606 mg; methyl 3-methyl-2-(2-phenylethynyl)benzoate, 626 mg; methyl 2-(2-*p*-tolylethynyl)benzoate, 626 mg; methyl 2-[(1-cyclohexenyl)ethynyl]benzoate, 601 mg; methyl 2-[2-(trimethylsilyl)ethynyl]benzoate, 581 mg] and 1 N NaOH (14.0 mL) in THF (3.0 mL) was heated at 50 °C for 12 h. After cooling to room temperature, the mixture was washed with Et_2O (3 × 15 mL), further cooled with the aid of an ice bath, and neutralized with 1 N HCl. The resulting mixture was extracted at room temperature with CH_2Cl_2 (3 × 50 mL), and the collected organic layers dried over Na_2SO_4. Filtration and evaporation of the solvent afforded the crude 2-alkynylbenzoic acid derivatives (in the case of methyl 2-[2-(trimethylsilyl)ethynyl]benzoate, triple bond deprotection also occurred together with ester hydrolysis to give 2-ethynylbenzoic acid). 2-(Hex-1-ynyl)benzoic acid **1c** was a low melting yellowish solid, and was sufficiently pure to be used as such in the iodocyclization reactions. All other 2-alkynylbenzoic acids **1a**,**b** and **1d**-**i** and 2-ethynylbenzoic acid **1j** were further purified by crystallization with Et_2O/hexane.

*2-(3,3-Dimethylbut-1-ynyl)benzoic acid (**1a**).* Yield: 420 mg, starting from 541 mg of methyl 2-(3,3-dimethylbut-1-ynyl)benzoate (83%). White solid, mp = 116-118 °C, lit.,[13] 118-122 °C. IR (KBr): ν = 3074 (w), 2966 (m), 2243 (w), 1695 (s), 1566 (w), 1486 (m), 1412 (m), 1297 (m), 1267 (s), 1087 (w), 938 (m), 756 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 12.57 (s, br, 1 H), 8.06 (dd, J = 7.9, 1.2, 1 H), 7.52 (distorted dd, J = 7.9, 1.2, 1 H), 7.46 (td, J = 7.3, 1.2, 1 H), 7.34

(td, *J* = 7.3, 1.2, 1 H), 1.36 (s, 9 H); ^{13}C NMR (126 MHz, CDCl$_3$): *δ* = 171.7, 134.1, 132.3, 131.1, 130.9, 127.3, 124.9, 105.1, 77.8, 30.7, 28.3; LC-MS: *m/z* =225.09 [(M+Na)$^+$]; anal. calcd for $C_{13}H_{14}O_2$ (202.25): C, 77.20; H, 6.98; found C, 77.22; H, 6.96. The spectroscopic data were in good agreement with those reported.[13]

*5-Chloro-2-(3,3-dimethylbut-1-ynyl)benzoic acid (**1b**).* Yield: 472 mg, starting from 627 mg of methyl 5-chloro-2-(3,3-dimethylbut-1-ynyl)benzoate (80%). White solid, mp = 112-113 °C. IR (KBr): *ν* = 3075 (w), 2964 (m), 2240 (w), 1705 (s), 1480 (w), 1438 (m), 1415 (m), 1298 (s), 1252 (s), 1112 (m), 830 (w), 718 (w) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): *δ* = 11.35 (s, br, 1 H), 8.05-8.01 (m, 1 H), 7.46-7.42 (m, 2 H), 1.35 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$): *δ* = 170.4, 135.3, 133.2, 132.5, 132.0, 131.1, 123.5, 106.2, 76.9, 30.6, 28.4; LC-MS: *m/z* = 275.01 [(M+K)$^+$]; anal. calcd for $C_{13}H_{13}ClO_2$ (236.69): C, 65.97; H, 5.54; Cl, 14.98; found C, 65.95; H, 5.55; Cl, 14.96.

*2-(Hex-1-ynyl)benzoic acid (**1c**).* Yield: 320 mg, starting from 541 mg of methyl 2-(hex-1-ynyl)benzoate (63%). Low-melting colorless solid. IR (film): *ν* = 2957 (w), 1691 (s), 1575 (w), 1411 (m), 1271 (s), 920 (m), 740 (m), 664 (w) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): *δ* = 11.96 (s, br, 1 H), 8.06 (distorted dd, *J* = 7.8, 1.0, 1 H), 7.54 (distorted dd, *J* = 7.7, 1.1, 1 H), 7.47 (td, *J* = 7.7, 1.2, 1 H), 7.35 (td, *J* = 7.7, 1.1, 1 H), 2.50 (t, *J* = 6.8, 2 H), 1.70 -1.45 (m, 4 H), 0.96 (t, *J* = 7.2, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): *δ* = 171.6, 134.4, 132.4, 131.1, 130.7, 127.3, 125.0, 97.4, 79.1, 30.6, 22.0, 19.5, 13.6.; LC-MS *m/z* = 225.09 [(M+Na)$^+$]; anal. calcd for $C_{13}H_{14}O_2$ (202.25): C, 77.20; H, 6.98; found C, 77.17; H, 6.95. The spectroscopic data agreed with those reported.[10]

*2-(2-Phenylethynyl)benzoic acid (**1d**).* Yield: 497 mg, starting from 591 mg of methyl 2-(2-phenylethynyl)benzoate (89%). Yellow solid, mp = 126-127 °C, lit.[14] 126-127 °C. IR (KBr): *ν* = 2216 (w), 1694 (s), 1564 (m), 1494 (m), 1480 (m), 1419 (m), 1298 (m), 1271 (s), 1159 (w), 1079 (w), 917 (m), 751 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): *δ* = 11.26 (s, br, 1 H), 8.13 (dd, *J* = 7.9, 1.2, 1 H), 7.68 (distorted dd, *J* = 7.8, 1.1, 1 H), 7.61-7.50 (m, 3 H), 7.40 (td, *J* = 7.6, 1.2, 1 H), 7.33-7.25 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.8, 134.2, 132.6, 131.8, 131.4, 130.5, 128.6, 128.4, 127.9, 124.5, 123.2, 95.3, 88.1; LC-MS *m/z* = 245.06 [$(M+Na)^+$]; anal. calcd for $C_{15}H_{10}O_2$ (222.24): C, 81.07; H, 4.54; found C, 81.09; H, 4.53. The spectroscopic data were in good agreement with those reported.[14]

*5-Chloro-2-(2-phenylethynyl)benzoic acid (**1e**).* Yield: 526 mg, starting from 677 mg of methyl 5-chloro-2-(2-phenylethynyl)benzoate (82%). White solid, mp = 138-139 °C. IR (KBr): *v* = 3083 (m, br), 2218 (w), 1697 (s), 1494 (w), 1475 (w), 1302 (m), 1252 (m), 1107 (m), 835 (w), 787 (w), 751 (m), 685 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.03 (s, br, 1 H), 8.12-8.06 (m, 1 H), 7.66-7.46 (m, 4 H), 7.37-7.25 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.4, 135.3, 134.0, 132.8, 131.8, 131.4, 130.2, 128.8, 128.5, 123.1, 122.9, 96.4, 87.1; LC-MS *m/z* = 257.04 [$(M+H)^+$]; anal. calcd for $C_{15}H_9ClO_2$ (256.68): C, 70.19; H, 3.53; Cl, 13.81; found C, 70.21; H, 3.52; Cl, 13.80.

*2-(2-Thiophen-3-yl)ethynyl]benzoic acid (**1f**).* Yield: 470 mg, starting from 606 mg of methyl 2-[2-(thiophen-3-yl)ethynyl]benzoate (82%). Yellow solid, mp = 53-54 °C. IR (KBr): *v* = 2828 (w, br), 2212 (vw), 1678 (s), 1567 (w), 1408 (w), 1307 (m), 1284 (m), 1262 (m), 1077 (w), 934 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.18 (s, br, 1 H), 8.12 (distorted d, *J* = 7.8, 1 H), 7.65 (distorted d, *J* = 7.7, 1 H), 7.59-7.48 (m, 2 H), 7.40 (td, *J* = 7.8, 1.1, 1 H), 7.29-7.19 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.4, 134.1, 132.6, 131.3, 130.5, 129.9, 129.3, 127.9, 125.4, 124.5, 122.3, 90.5, 87.7; LC-MS: *m/z* = 251.01 [$(M+Na)^+$]; anal. calcd for $C_{13}H_8O_2S$ (228.27): C, 68.40; H, 3.53; S, 14.05; found C, 68.41; H, 3.55; S, 14.03.

*3-Methyl-2-(2-phenylethynyl)benzoic acid (**1g**).* Yield: 498 mg, starting from 626 mg of methyl 3-methyl-2-(2-phenylethynyl)benzoate (84%). White solid, mp = 72-73 °C. IR (KBr): *v* =

2969 (m, br), 2209 (w), 1683 (s), 1441 (w), 1412 (w), 1295 (m), 1267 (m), 759 (m), 691 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 11.60 (s, br, 1 H), 7.98-7-91 (m, 1 H), 7.61-7.53 (m, 2 H), 7.48-7.42 (m, 1 H), 7.33-7-23 (m, 4 H), 2.59 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ =172.3, 142.1, 133.8, 131.6, 131.1, 128.7, 128.5, 128.4, 127.4, 123.7, 123.4, 100.4, 86.5, 21.3; LC-MS *m/z* = 237.09 [(M+H)$^+$]; anal. calcd for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12; found C, 81.32; H, 5.14.

*2-p-Tolylethynylbenzoic acid (**1h**).* Yield: 504 mg, starting from 626 mg of methyl 2-(2-*p*-tolylethynyl)benzoate (85%). White solid, mp = 117-118 °C, lit.,[10] 98-100 °C. IR (KBr): *ν* = 3417 (w, br), 2216 (w), 1696 (s), 1511 (w), 1412 (w), 1300 (m), 1268 (m), 932 (w), 816 (m), 756 (m) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ = 11.64 (s, br, 1 H), 8.12 (d, *J* = 7.3, 1 H), 7.66 (distorted d, *J* = 7.9, 1 H), 7.52 (td, *J* = 7.3, 1.2, 1 H), 7.46 (d, *J* = 7.9, 2 H), 7.39 (td, *J* = 7.9, 1.2, 1 H), 7.08 (d, *J* = 7.9, 2 H), 2.32 (s, 3 H); ^{13}C NMR (126 MHz, CDCl$_3$): δ = 171.7, 138.8, 134.1, 132.6, 131.7, 131.4, 130.5, 129.2, 127.7, 124.7, 120.2, 95.7, 87.6, 21.5; LC-MS *m/z* = 259.08 [(M+Na)$^+$]; anal. calcd for $C_{16}H_{12}O_2$ (236.27): C, 81.34; H, 5.12; found C, 81.37; H, 5.10. The spectroscopic data agreed with those reported.[10,15]

*2-[(1-Cyclohexenyl)ethynyl]benzoic acid (**1i**).* Yield: 480 mg, starting from 601 mg of methyl 2-[(1-cyclohexenyl)ethynyl]benzoate (85%). Yellow solid, mp = 75-76 °C. IR (KBr): ν = 2935 (m, br), 2197 (w), 1698 (s), 1592 (w), 1435 (w), 1414 (m), 1315 (m), 1287 (m), 1078 (w), 920 (m), 752 (m), 656 (m) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 11.71 (s, br, 1 H), 8.08 (dd, *J* = 7.9, 0.8, 1 H), 7.56 (distorted dd, *J* = 7.7, 0.8, 1 H), 7.53-7.45 (m, 1 H), 7.41-7.32 (m, 1 H), 6.34-6.26 (m, 1 H), 2.33-2.22 (m, 2 H), 2.22-2.11 (m, 2 H), 1.76-1.56 (m, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 171.6, 136.4, 134.0, 132.4, 131.2, 130.3, 127.4, 124.8, 120.9, 97.5, 85.5, 28.8, 25.9, 22.3, 21.5; LC-MS *m/z* = 249.09 [(M+Na)$^+$]; anal. calcd for $C_{15}H_{14}O_2$ (226.27): C, 79.62; H, 6.24; found C, 79.64; H, 6.21. The spectroscopic properties agreed with those previously reported.[11]

*2-Ethynylbenzoic acid (**1j**).* Yield: 220 mg, starting from 581 mg of methyl 2-[2-(trimethylsilyl)ethynyl]benzoate (60%). Yellow solid, mp = 120-122 °C lit.,[14] 121-123 °C. IR (KBr): v = 3291 (w), 1696 (s), 1595 (w), 1569 (w), 1489 (m), 1406 (m), 1279 (s), 1080 (w), 919 (m), 827 (w), 757 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.62 (s, br, 1 H), 8.09 (distorted d, J = 7.9, 1 H), 7.66 (distorted d, J = 7.7, 1 H), 7.53 (t, J = 7.6, 1 H), 7.44 (distorted t, J = 7.6, 1 H), 3.46 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.4, 135.2, 132.6, 131.3, 131.2, 128.6, 123.2, 83.3, 81.8; LC-MS m/z = 169.02 [(M+Na)$^+$]; anal. calcd for $C_9H_6O_2$ (146.14): C, 73.97; H, 4.14; found C, 73.99; H, 4.16. The spectroscopic properties agreed with those previously reported.[14]

X-ray Crystallographic Data Collection and Structure Refinement for Compounds 2a and 3d

Single-crystal X-ray diffraction data for compounds **2a** and **3d** were collected at room temperature on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Suitable, needle-like shaped (**2a**) and laminar (**3d**) crystals of approximate dimensions 0.20 × 0. 06 × 0.05 and 0.18 × 0.06 × 0.02 mm^3, respectively, were selected for data collection. The data were processed through the SAINT[16] reduction and SADABS[17] multi-scan absorption software. The structures were solved with the ShelXS structure solution program. In both cases, the model was refined by using version 2013/4 of ShelXL against F^2 on all data by full-matrix least squares.[18] Compound **3d**, which crystallizes in the monoclinic space group *C*2, was refined as a racemic twin. The final geometrical calculations and the graphical manipulations were performed using the XP utility within the SHELXTL software. Please note that despite all efforts, a low $\theta_{\max}$ of diffraction was obtained for **3d**, due to poor crystal quality. Since the solution and refinement parameters in the final model are reasonable, we are confident that the crystal structure found for this compound is chemically reliable, although not perfect. ORTEP drawings of **2a** and **3d** are given in Figures S1 and S2 while details of the crystal data/data collection/structure refinement and selected bond lengths and angles are listed in Tables S1-S4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited within the Cambridge Crystallographic Data Centre as supplementary publication CCDC numbers 1502423 (**2a**) and 1502422 (**3d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

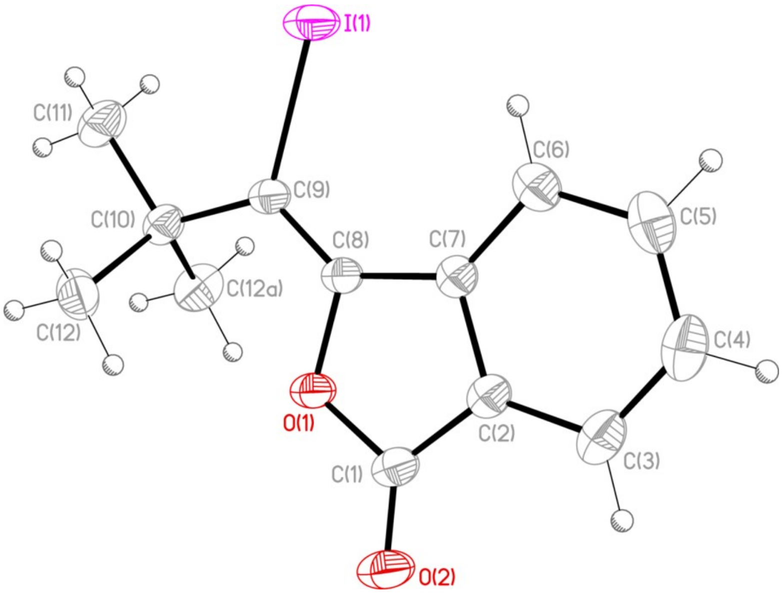

Figure S1. ORTEP drawing of the molecular structure of **2a**. Thermal ellipsoids have been depicted at 30% probability level. Symmetry code: (a) *x*, 0.5-*y*, *z*

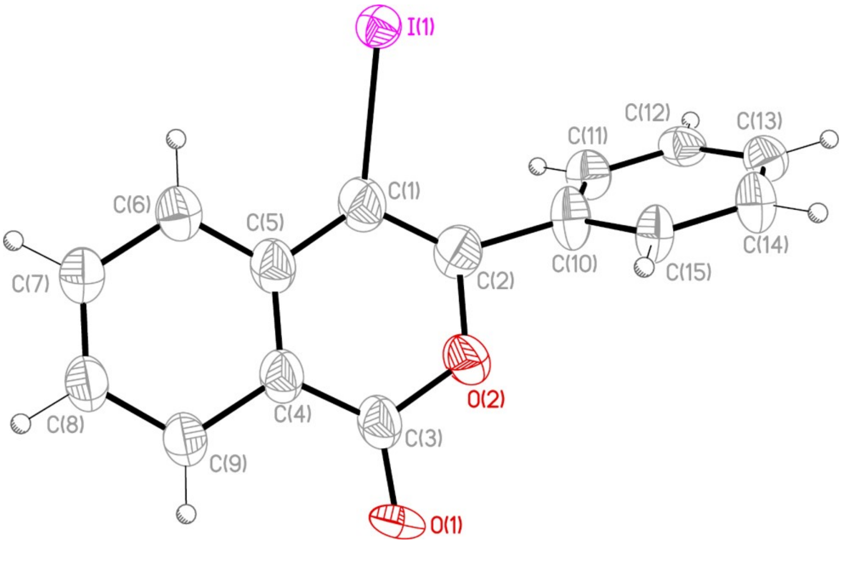

Figure S2. ORTEP drawing of the molecular structure of **3d**. Thermal ellipsoids have been depicted at 30% probability level.

Table S1. Crystal data and structure refinement for 2a.

Empirical formula	C_{13} H_{13} I O_2	
Formula weight	328.13	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*P n m a*	
Unit cell dimensions	a = 13.9685(19) Å	α = 90°
	b = 7.1901(9) Å	β = 90°
	c = 12.5256(16) Å	γ = 90°
Volume	1258.0(3) Å^3	
Z	4	
Density (calculated)	1.733 Mg/m^3	
Absorption coefficient	2.529 mm^{-1}	
F(000)	640	
Crystal size	0.200 x 0.060 x 0.050 mm^3	
Theta range for data collection	2.184 to 25.345°.	
Index ranges	-16<=h<=16, -8<=k<=8, -15<=l<=15	
Reflections collected	22340	
Independent reflections	1204 [R(int) = 0.0242]	
Completeness to theta = 25.242°	96.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1204 / 0 / 95	
Goodness-of-fit on F^2	1.339	
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0318, wR_2 = 0.0856	
R indices (all data)	R_1 = 0.0353, wR_2 = 0.1048	
Extinction coefficient	0.070(7)	
Largest diff. peak and hole	0.937 and -0.388 e.Å^{-3}	

Table S2. Crystal data and structure refinement for 3d.

Empirical formula	$C_{15} H_9 I O_2$	
Formula weight	348.12	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2	
Unit cell dimensions	a = 18.8983(13) Å	α = 90°.
	b = 5.7625(4) Å	β = 116.426(8)°.
	c = 13.2709(12) Å	γ = 90°.
Volume	1294.21(19) Å^3	
Z	4	
Density (calculated)	1.787 Mg/m^3	
Absorption coefficient	2.464 mm^{-1}	
F(000)	672	
Crystal size	0.180 x 0.060 x 0.020 mm^3	
Theta range for data collection	1.714 to 23.321°.	
Index ranges	-20<=h<=20, -6<=k<=6, -14<=l<=14	
Reflections collected	7989	
Independent reflections	1877 [R(int) = 0.0326]	
Completeness to theta = 25.242°	80.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1877 / 145 / 140	
Goodness-of-fit on F^2	1.129	
Final *R* indices [I>2sigma(I)]	R_1 = 0.0629, wR_2 = 0.1764	
R indices (all data)	R_1 = 0.0724, wR_2 = 0.1954	
Absolute structure parameter	0.46(17)	
Largest diff. peak and hole	1.401 and -1.091 e.Å^{-3}	

Table S3. Bond lengths [Å] and angles [°] for 2a.[a]

I(1)-C(9)	2.108(4)	C(4)-C(5)	1.387(9)
O(1)-C(1)	1.374(5)	C(5)-C(6)	1.388(7)
O(1)-C(8)	1.416(5)	C(6)-C(7)	1.403(6)
O(2)-C(1)	1.201(6)	C(7)-C(8)	1.481(6)
C(1)-C(2)	1.472(6)	C(8)-C(9)	1.348(6)
C(2)-C(7)	1.394(6)	C(9)-C(10)	1.548(6)
C(2)-C(3)	1.405(6)	C(10)-C(11)	1.544(6)
C(3)-C(4)	1.378(8)	C(10)-C(12)	1.545(4)
C(1)-O(1)-C(8)	111.2(3)	C(2)-C(7)-C(8)	106.7(3)
O(2)-C(1)-O(1)	121.5(4)	C(6)-C(7)-C(8)	134.8(4)
O(2)-C(1)-C(2)	131.9(4)	C(9)-C(8)-O(1)	116.5(3)
O(1)-C(1)-C(2)	106.6(4)	C(9)-C(8)-C(7)	137.1(4)
C(7)-C(2)-C(3)	123.1(4)	O(1)-C(8)-C(7)	106.4(3)
C(7)-C(2)-C(1)	109.1(3)	C(8)-C(9)-C(10)	124.9(4)
C(3)-C(2)-C(1)	127.9(4)	C(8)-C(9)-I(1)	116.7(3)
C(4)-C(3)-C(2)	117.3(5)	C(10)-C(9)-I(1)	118.4(3)
C(3)-C(4)-C(5)	120.5(4)	C(11)-C(10)-C(12)	107.0(3)
C(4)-C(5)-C(6)	122.3(5)	C(12a)-C(10)-C(12)	111.3(4)
C(5)-C(6)-C(7)	118.4(5)	C(11)-C(10)-C(9)	113.8(4)
C(2)-C(7)-C(6)	118.5(4)	C(12)-C(10)-C(9)	108.9(2)

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[a] Symmetry transformation used to generate equivalent atoms: (a) *x*, 0.5-*y*, *z*

Table S4. Bond lengths [Å] and angles [°] for 3d.

I(1)-C(1)	2.262(6)	C(5)-C(6)	1.348(2)
O(1)-C(3)	1.289(15)	C(6)-C(7)	1.42(3)
C(1)-C(2)	1.3900	C(7)-C(8)	1.33(4)
C(1)-C(5)	1.3900	C(8)-C(9)	1.40(3)
C(2)-O(2)	1.3900	C(10)-C(11)	1.3900
C(2)-C(10)	1.553(4)	C(10)-C(15)	1.3900
O(2)-C(3)	1.3900	C(11)-C(12)	1.3900
C(3)-C(4)	1.3900	C(12)-C(13)	1.3900
C(4)-C(5)	1.3900	C(13)-C(14)	1.3900
C(4)-C(9)	1.439(3)	C(14)-C(15)	1.3900

C(2)-C(1)-C(5)	120.0	C(6)-C(5)-C(1)	116.59(13)
C(2)-C(1)-I(1)	110.72(6)	C(4)-C(5)-C(1)	120.0
C(5)-C(1)-I(1)	129.07(5)	C(5)-C(6)-C(7)	118.0(13)
C(1)-C(2)-O(2)	120.0	C(8)-C(7)-C(6)	121(3)
C(1)-C(2)-C(10)	137.90(14)	C(7)-C(8)-C(9)	123(3)
O(2)-C(2)-C(10)	101.95(15)	C(8)-C(9)-C(4)	117.0(13)
C(2)-O(2)-C(3)	120.0	C(11)-C(10)-C(15)	120.0
O(1)-C(3)-C(4)	125.6(9)	C(11)-C(10)-C(2)	119.0(3)
O(1)-C(3)-O(2)	114.4(9)	C(15)-C(10)-C(2)	121.0(3)
C(4)-C(3)-O(2)	120.0	C(12)-C(11)-C(10)	120.0
C(5)-C(4)-C(3)	120.0	C(11)-C(12)-C(13)	120.0
C(5)-C(4)-C(9)	118.07(14)	C(12)-C(13)-C(14)	120.0
C(3)-C(4)-C(9)	121.93(14)	C(15)-C(14)-C(13)	120.0
C(6)-C(5)-C(4)	123.41(13)	C(14)-C(15)-C(10)	120.0

Table of Absolute Energies (Hartrees) of the Optimized Structures

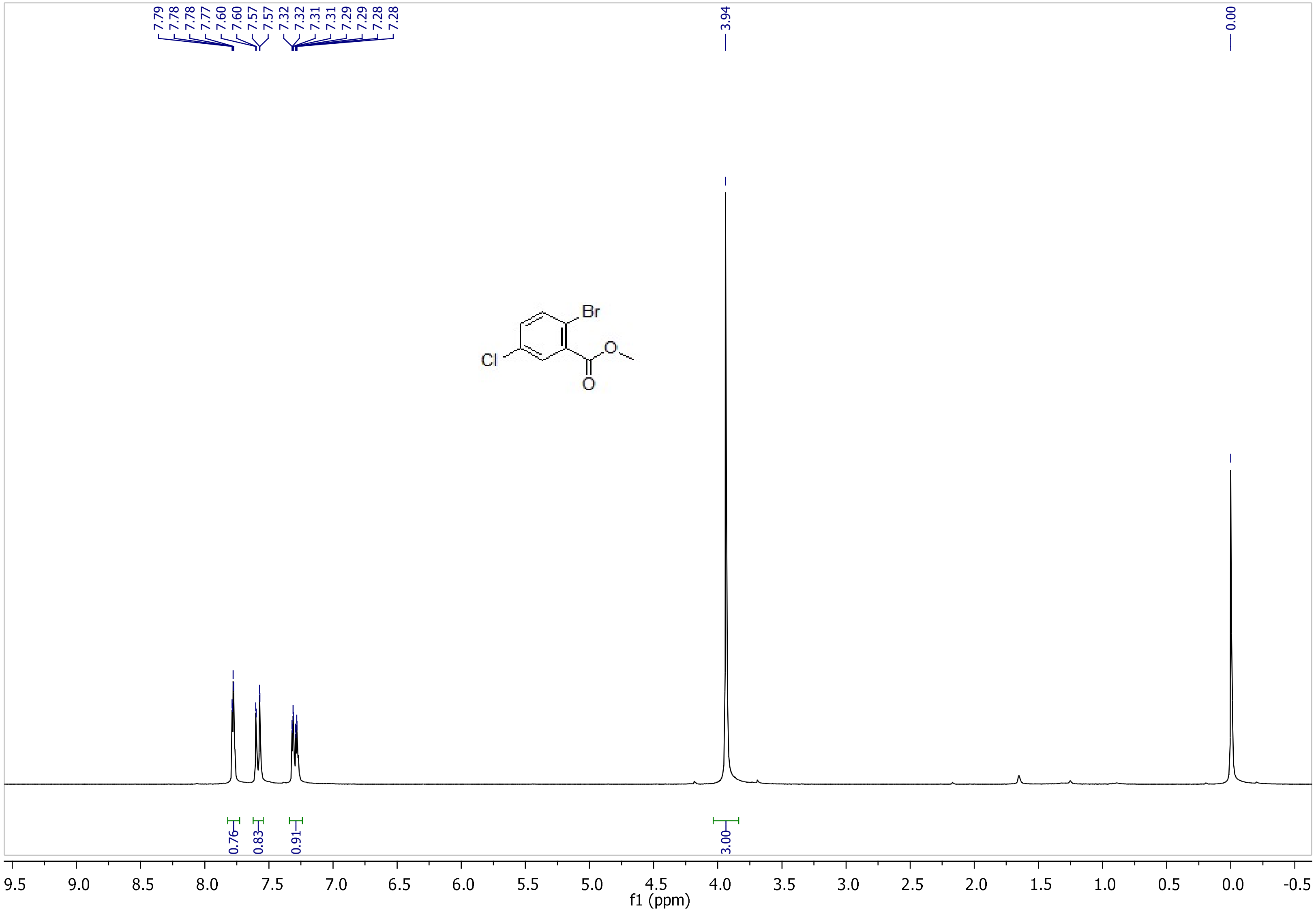
Table S5. Absolute energies in Hartrees of the optimized structures.

R	**structure**	**EmimEtSO$_4$**		**Mor$_{1,2}$N(CN)$_2$**	
		5	**6**	**5**	**6**
Ph	**ec**	-9549.5069276		-8535.2469935	
	1	-9549.5085442	-9549.5066856	-8535.2448210	-8535.2448210
	2	-9549.5068702	-9549.4996926	-8535.2349643	-8535.2349643
	3	-9549.5318358	-9549.5324885	-8535.2327681	-8535.2327681
	4	-9549.5341648	-9549.5480810	-8535.2636182	-8535.2636182
	5	-	-	-	-
	pc	-9549.5345656	-9549.5513714	-8535.2801029	-8535.2801029
H	**ec**	-9318.3541220		-8304.0893418	
	1	-9318.3570864	-9318.3542214	-8304.0862469	-8304.0852334
	2	-9318.3824165	-9318.3502709	-8304.0808407	-8304.0744745
	3	-9318.3878738	-9318.3510584	-8304.0828285	-8304.0732842
	4	-9318.3899666	-9318.3901944	-8304.0908753	-8304.0716060
	5	-	-	-8304.1153854	-8304.1073288
	pc	-9318.3918206	-9318.3959748	-8304.1227680	-8304.1298451
(CH$_3$)$_3$C	**ec**	-9475.6942156		-8461.4234163	
	1	-9475.6945466	-9475.6922481	-8461.4207025	-8461.4234145
	2	-9475.6900883	-9475.6867354	-8461.4102621	-8461.4202308
	3	-9475.6872934	-9475.6833318	-8461.4095081	-8461.4102558
	4	-9475.6900800	-9475.6833057	-8461.4116128	-8461.4028437
	5	-9475.7038377	-9475.7043557	-8461.4376085	-8461.4391429
	pc	-9475.7062075	-9475.7111239	-8461.4403696	-8461.4471972
C$_4$H$_3$S	**ec**	-9870.2707203		-8856.0054379	
	1	-9870.2681736	-9870.2697769	-8856.0034401	-8856.0054386
	2	-9870.2670577	-9870.2652821	-8855.9954208	-8856.0028393
	3	-9870.2808641	-9870.2663056	-8855.9971530	-8855.9916818
	4	-9870.2932781	-9870.2898354	-8856.0033068	-8855.9900878
	5	-	-	-8856.0281034	-8856.0166088
	pc	-9870.2949626	-9870.2984482	-8856.0335731	-8856.0361720

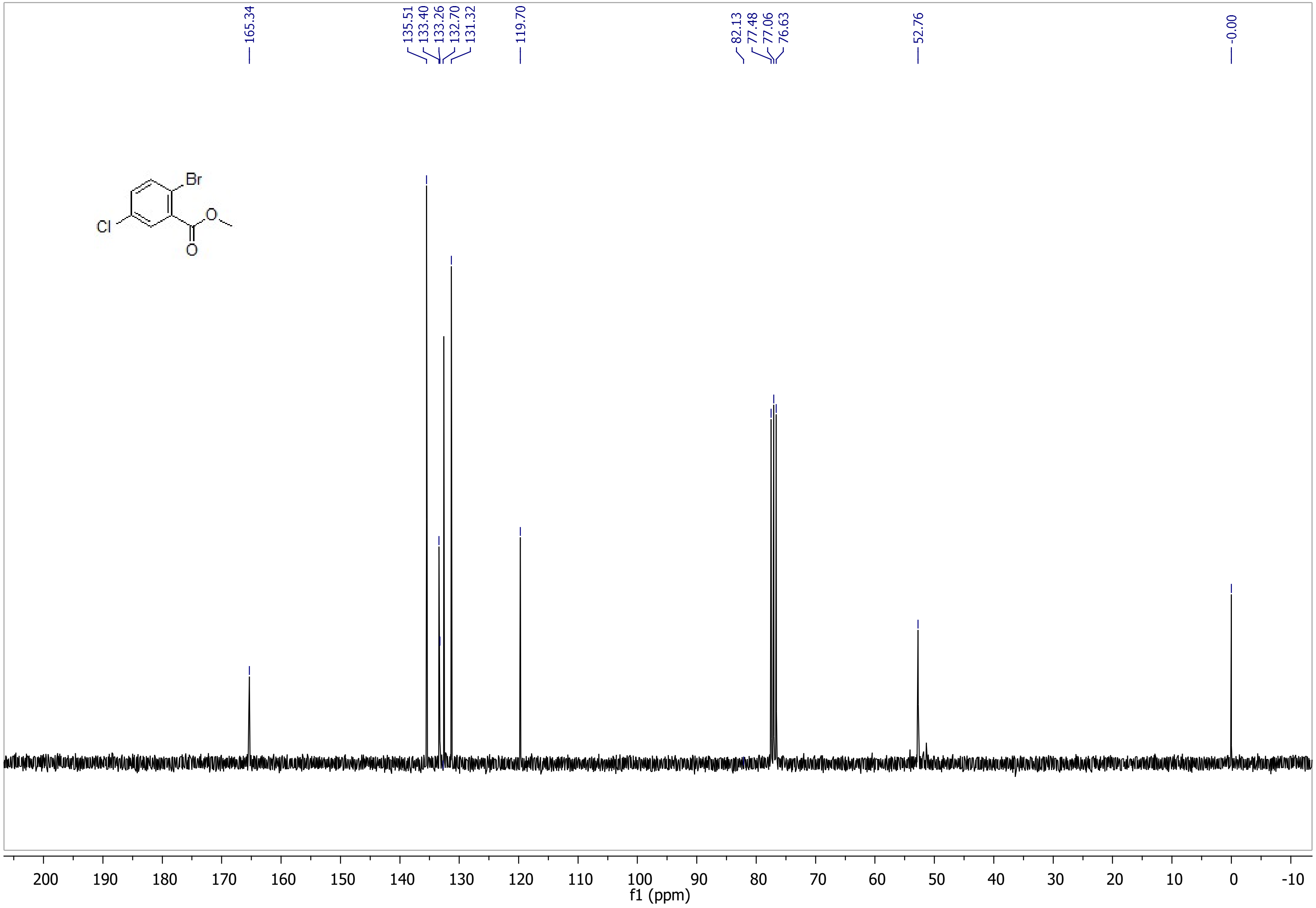
Copy of ^{1}H and ^{13}C NMR Spectra

Methyl 2-bromo-5-chlorobenzoate

^{1}H NMR($CDCl_3$)

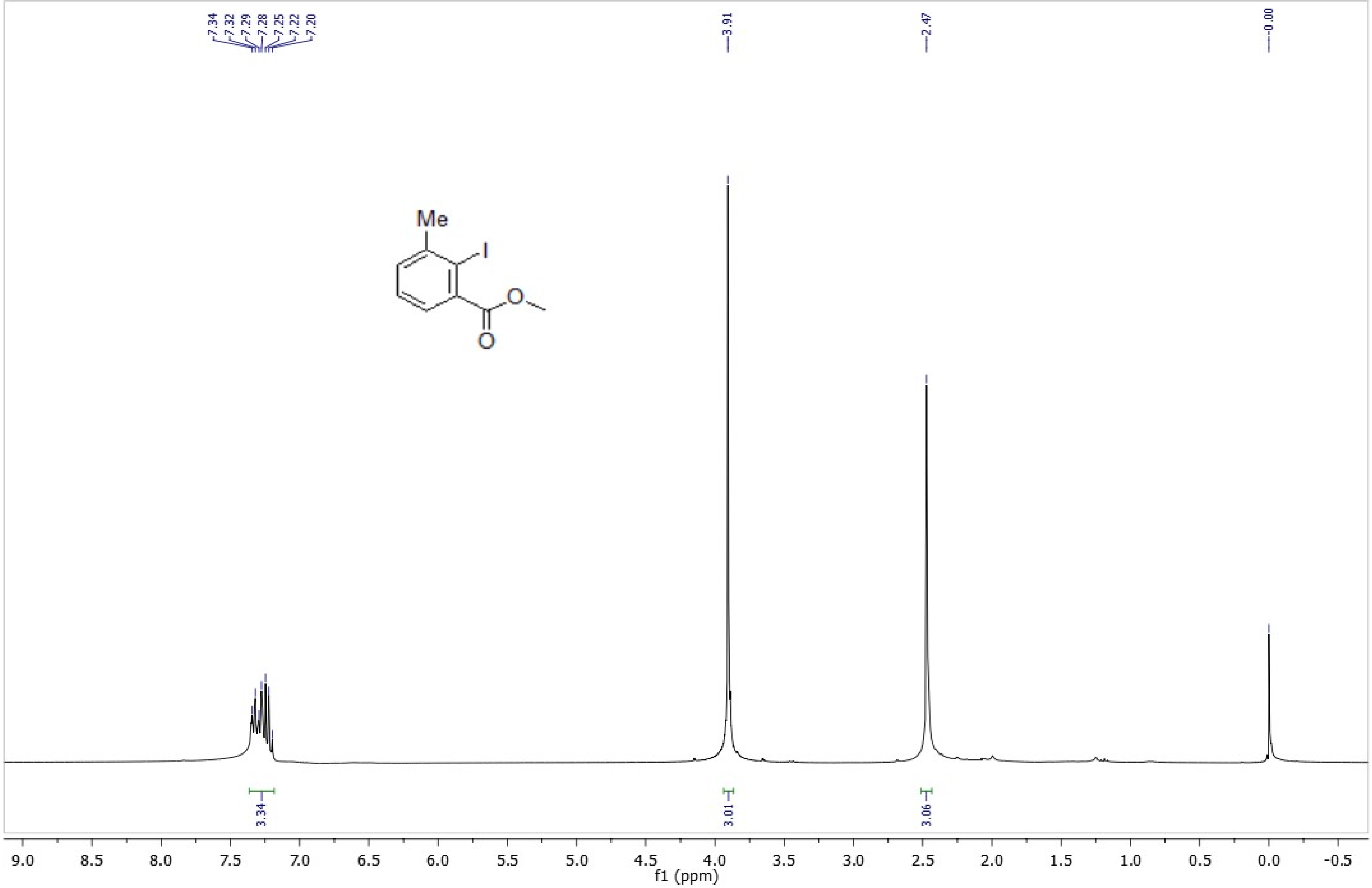


^{13}C NMR(CDCl$_3$)

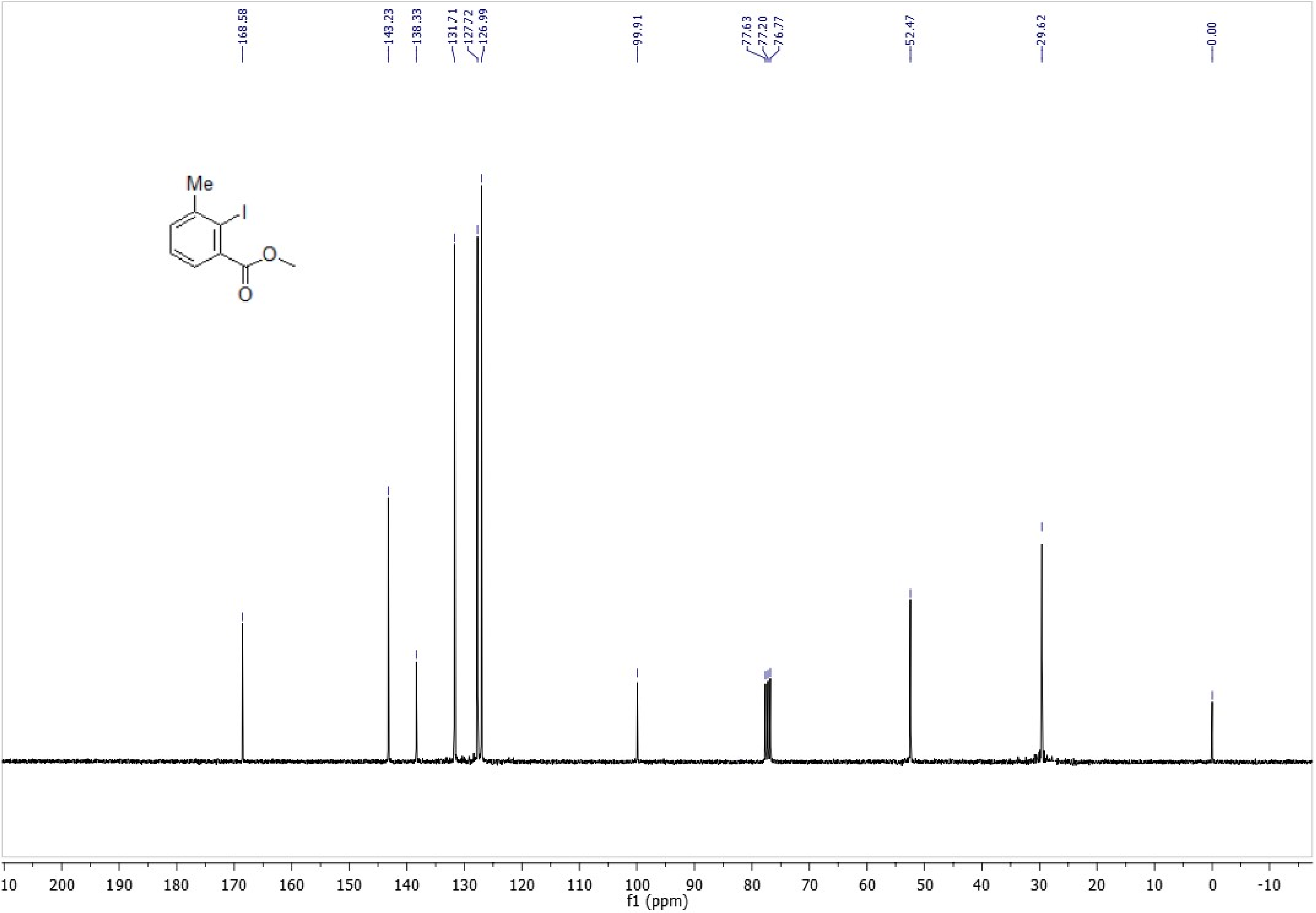


Methyl 3-methyl-2-iodobenzoate

^{1}H NMR($CDCl_3$)

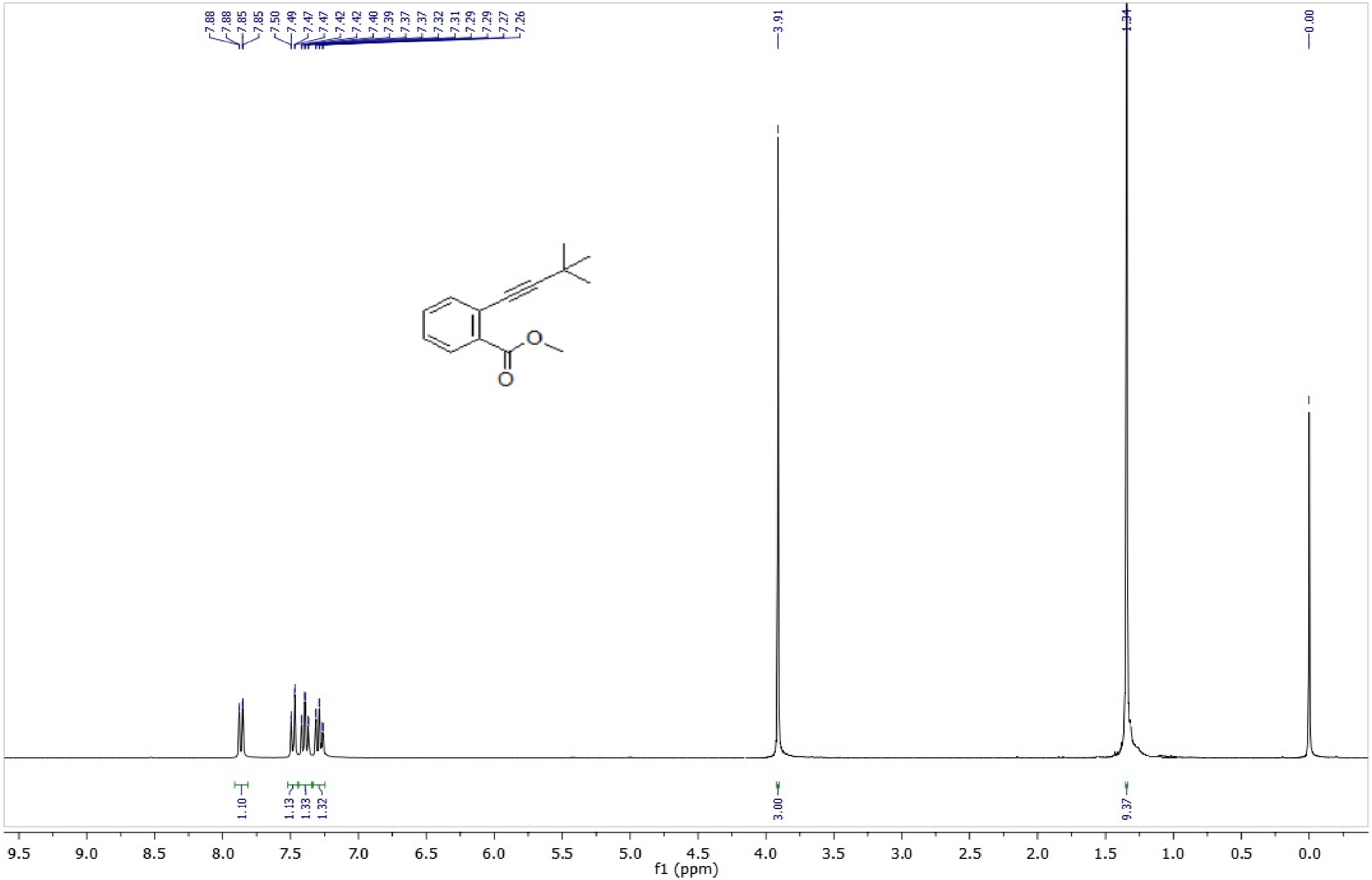


^{13}C NMR(CDCl$_3$)

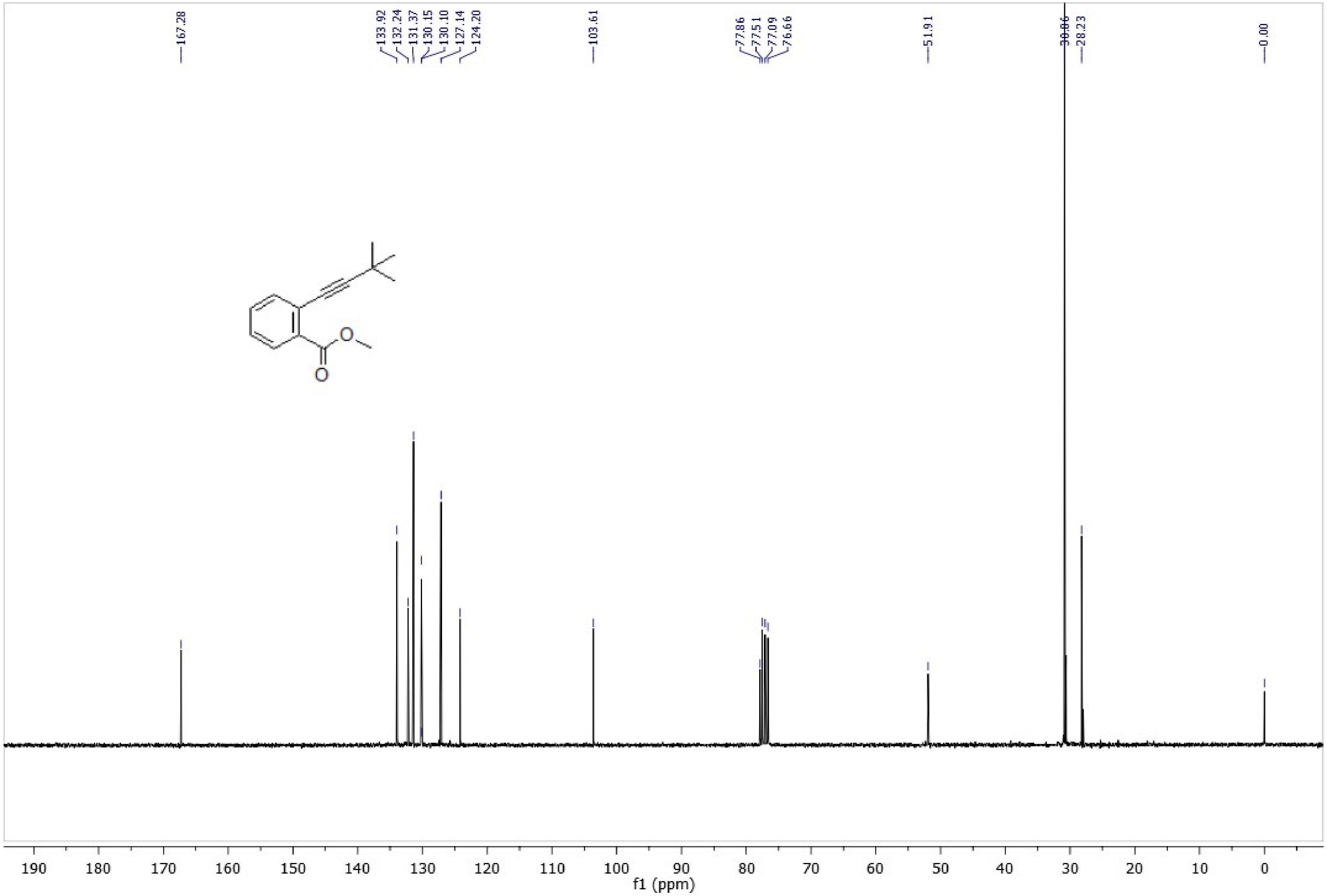


Methyl 2-(3,3-dimethylbut-1-ynyl)benzoate

^{1}H NMR(CDCl$_3$)

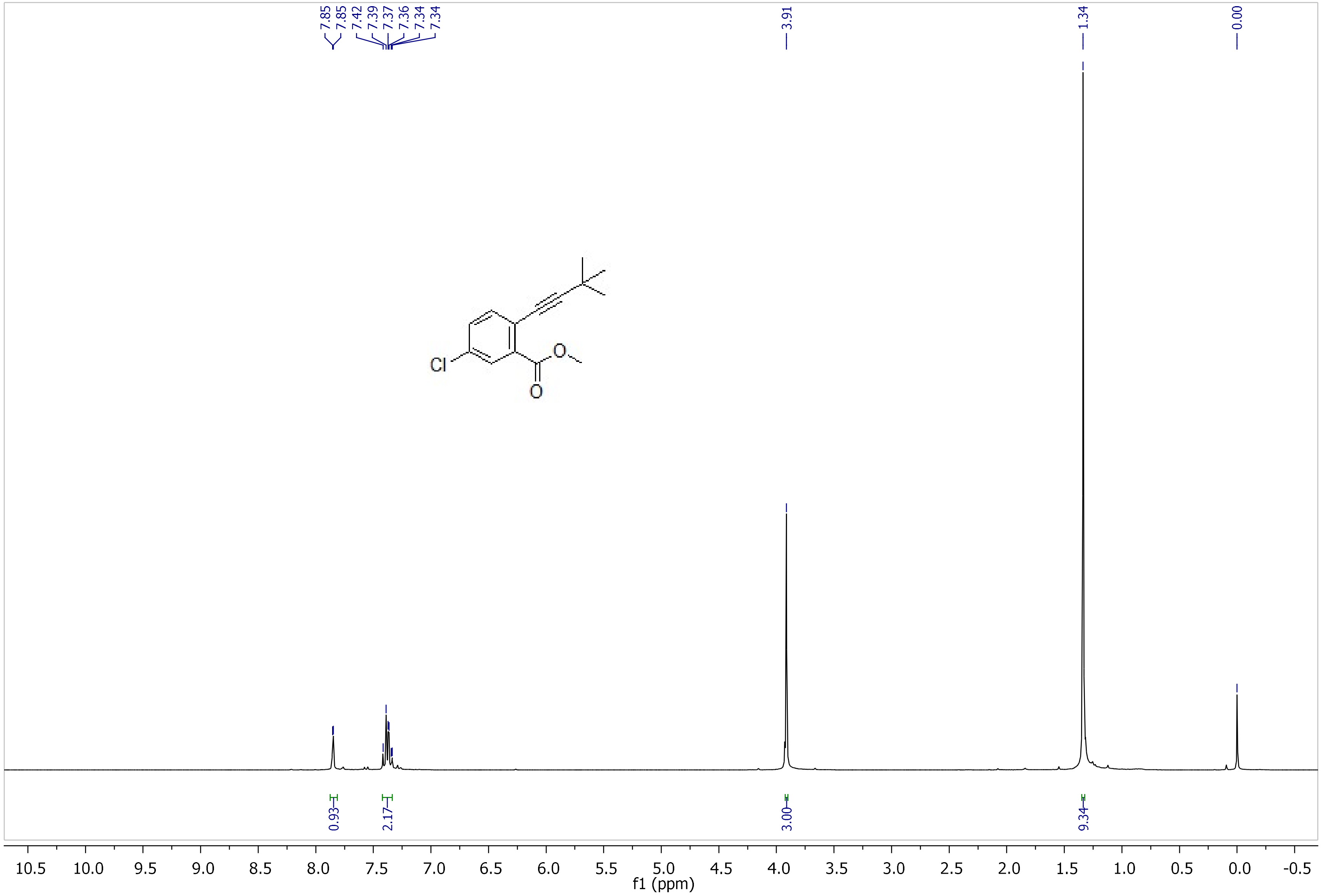


^{13}C NMR($CDCl_3$)

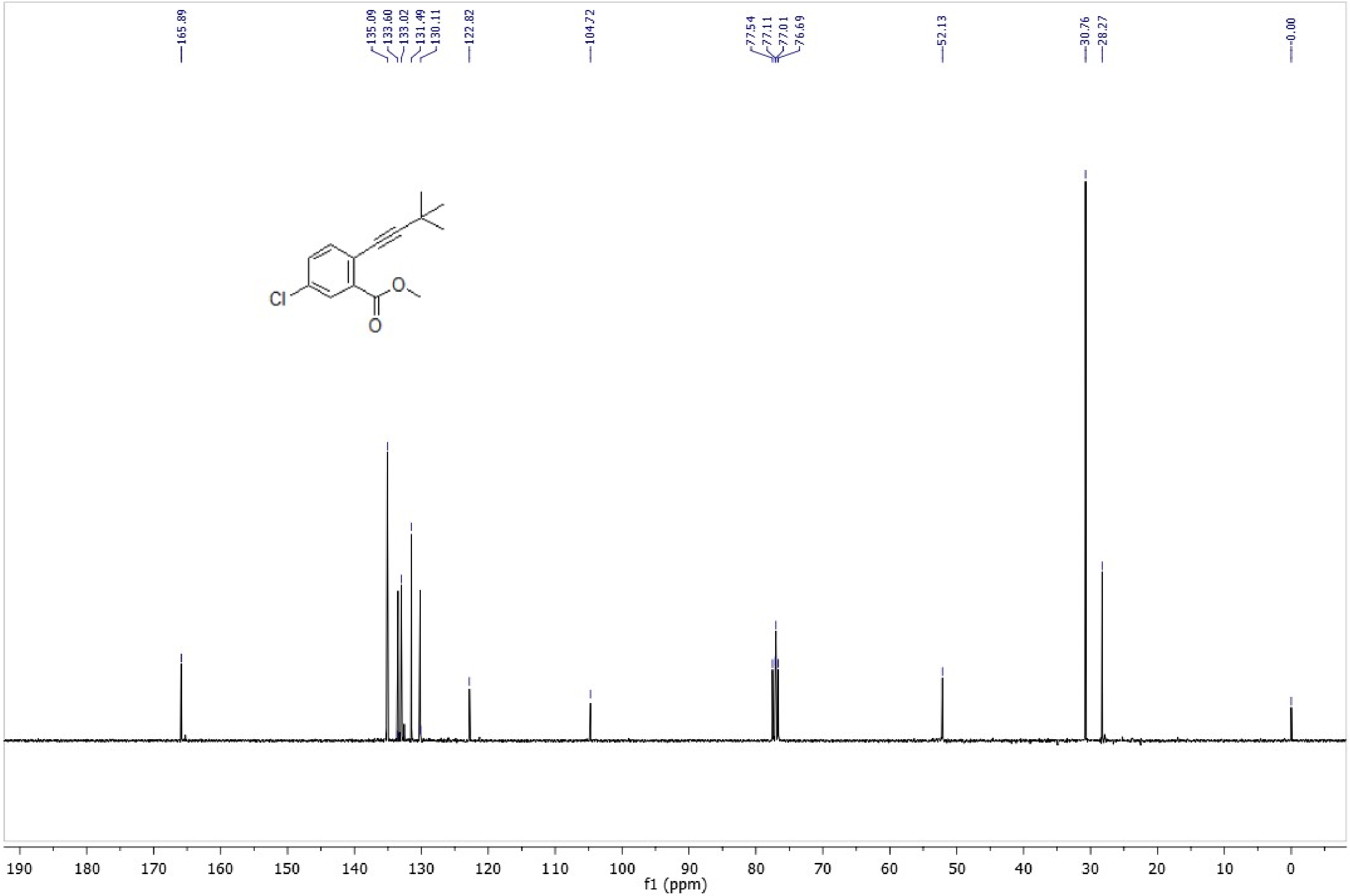


Methyl 5-chloro-2-(3,3-dimethylbut-1-ynyl)benzoate

^{1}H NMR(CDCl$_3$)

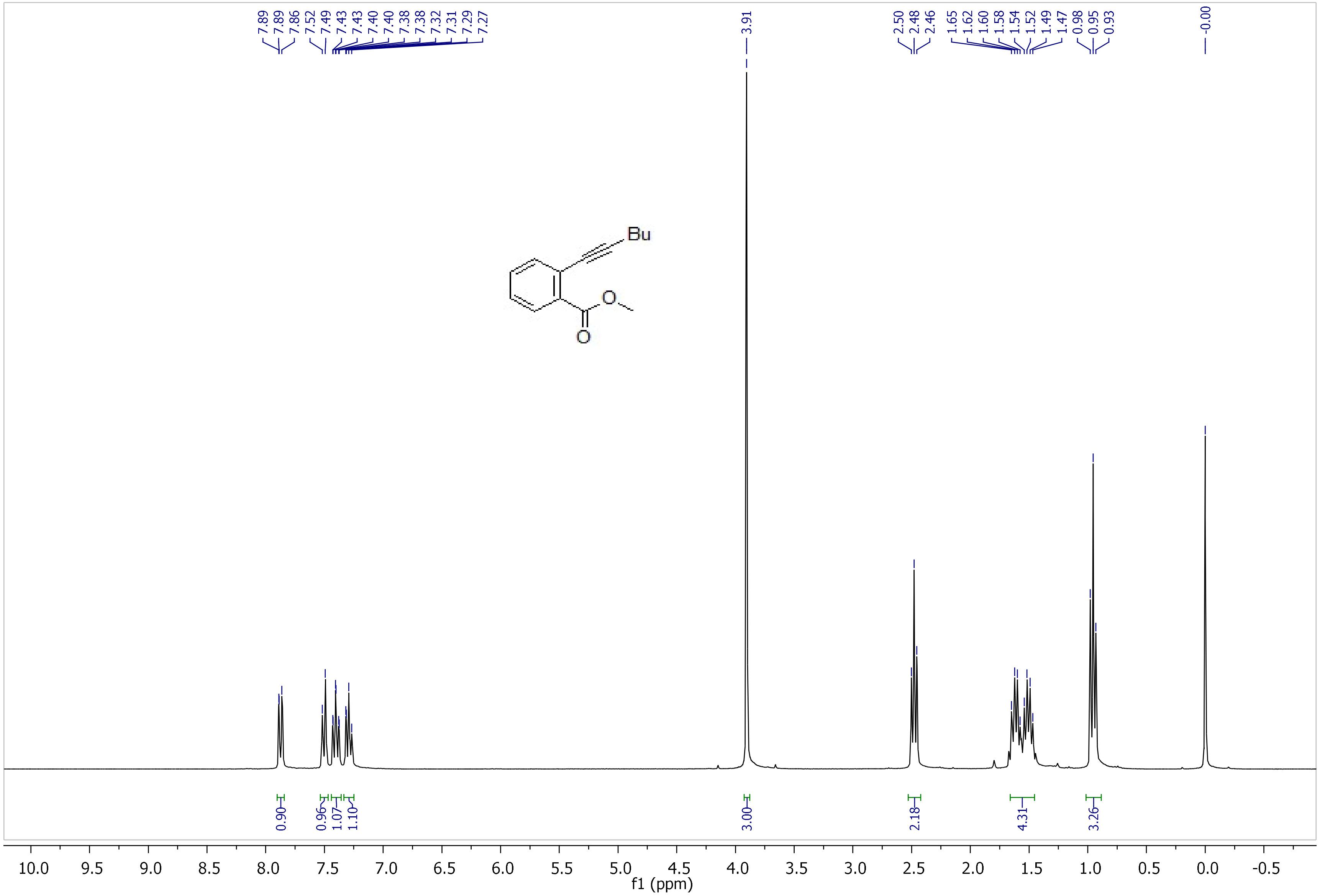


^{13}C NMR(CDCl$_3$)

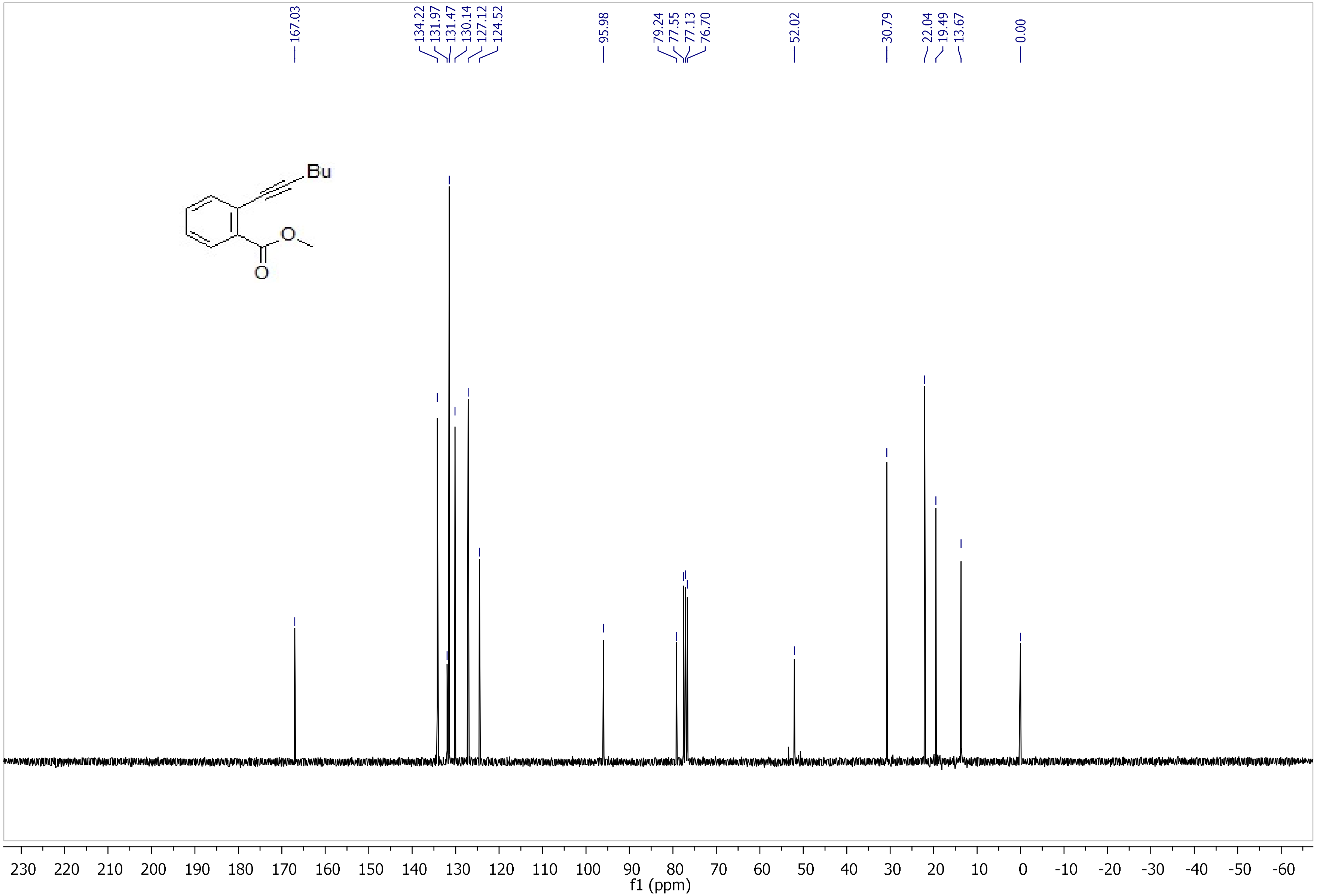


Methyl 2-(hex-1-ynyl)benzoate

^{1}H NMR($CDCl_3$)

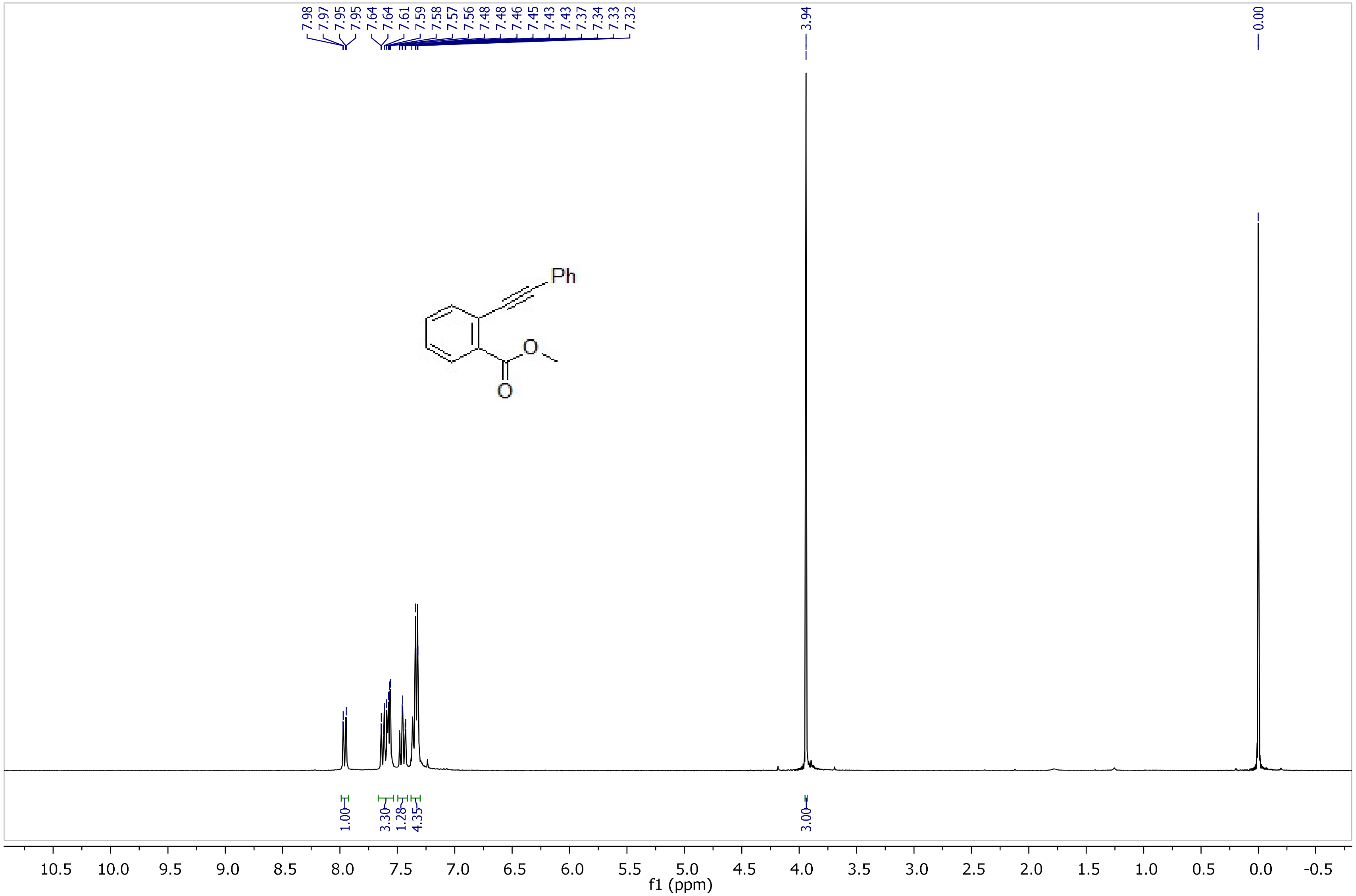


^{13}C NMR(CDCl$_3$)

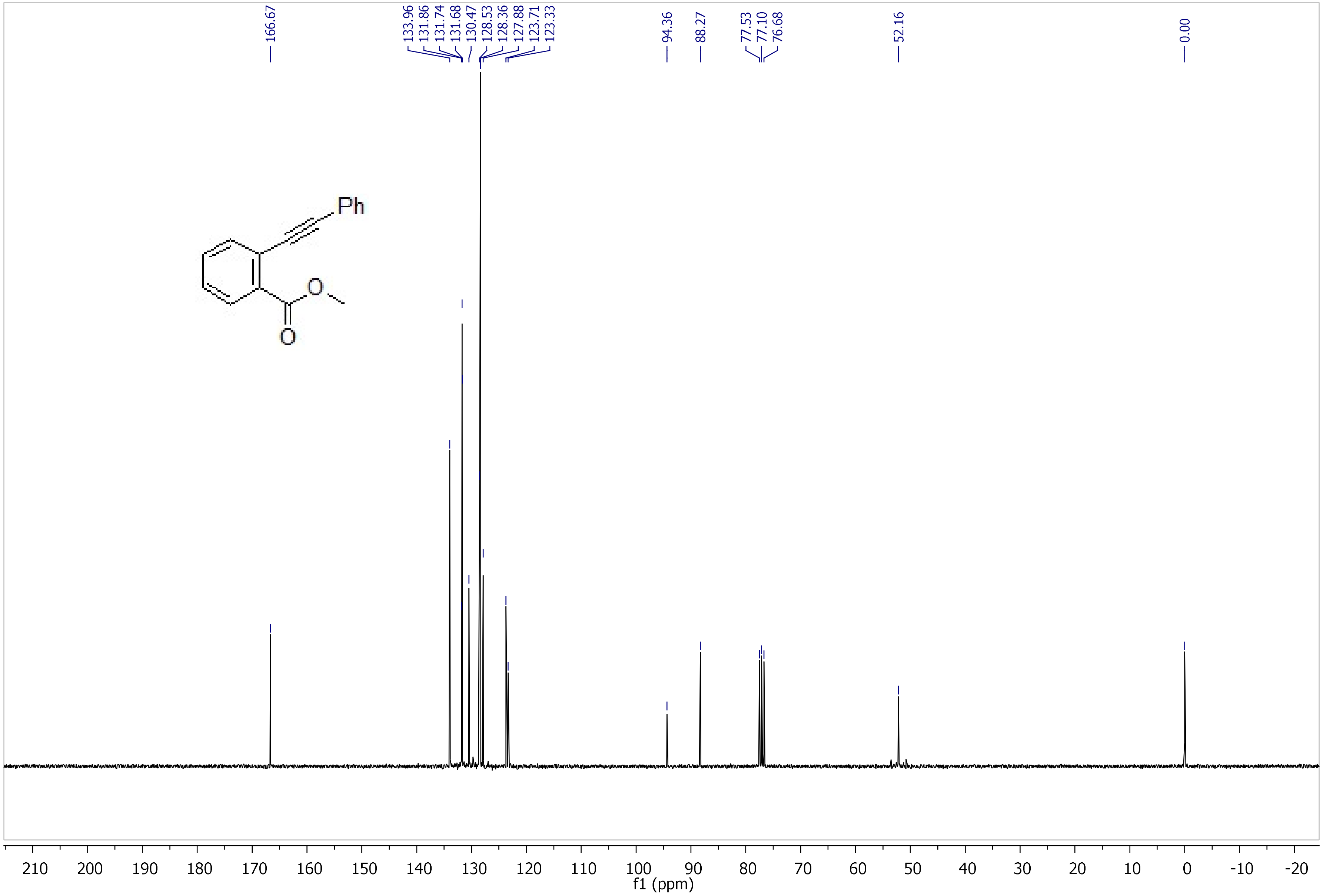


Methyl 2-(2-phenylethynyl)benzoate

^{1}H NMR(CDCl$_3$)

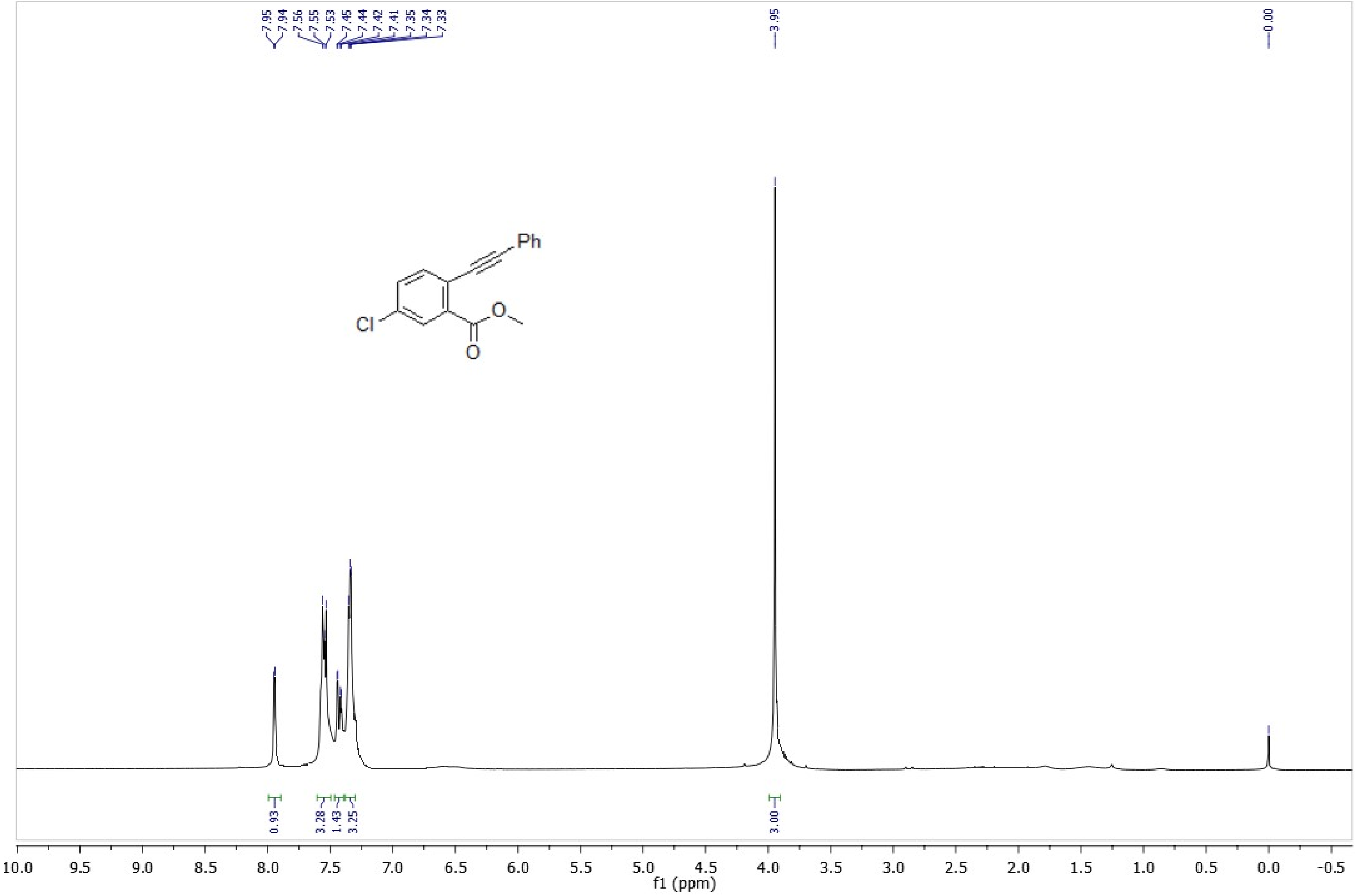


^{13}C NMR(CDCl$_3$)

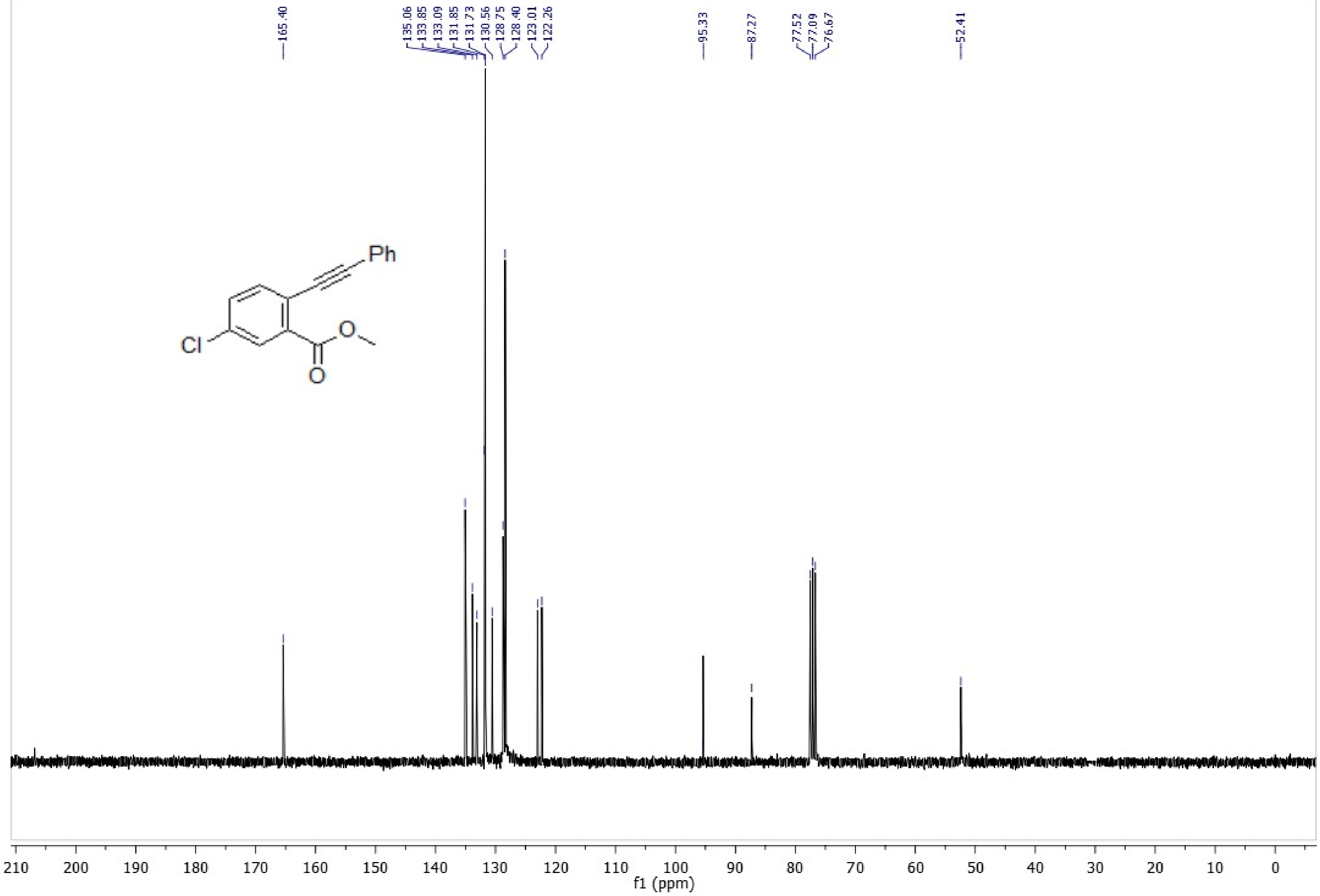


Methyl 5-chloro-2-(2-phenylethynyl)benzoate

^{1}H NMR(CDCl$_3$)

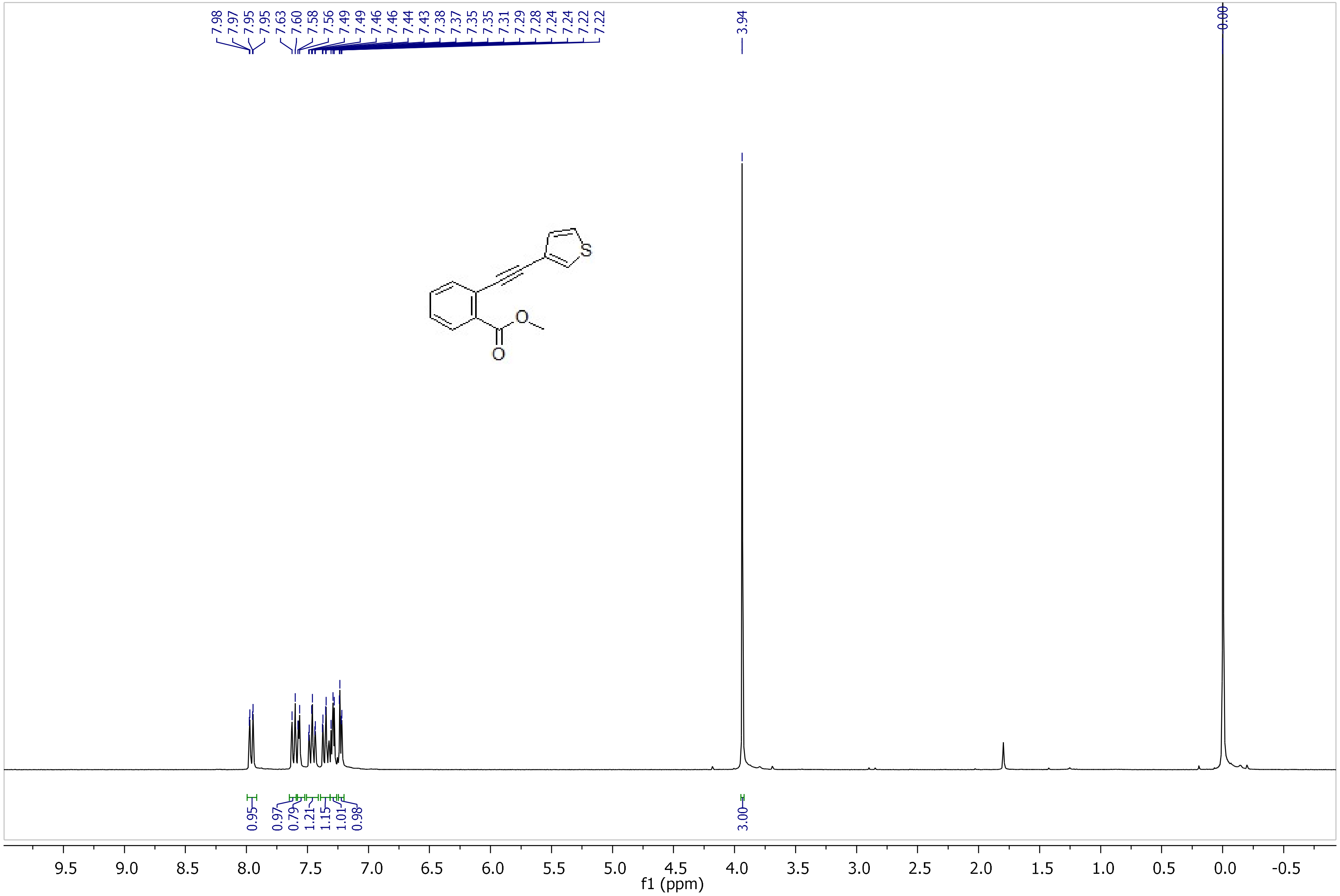


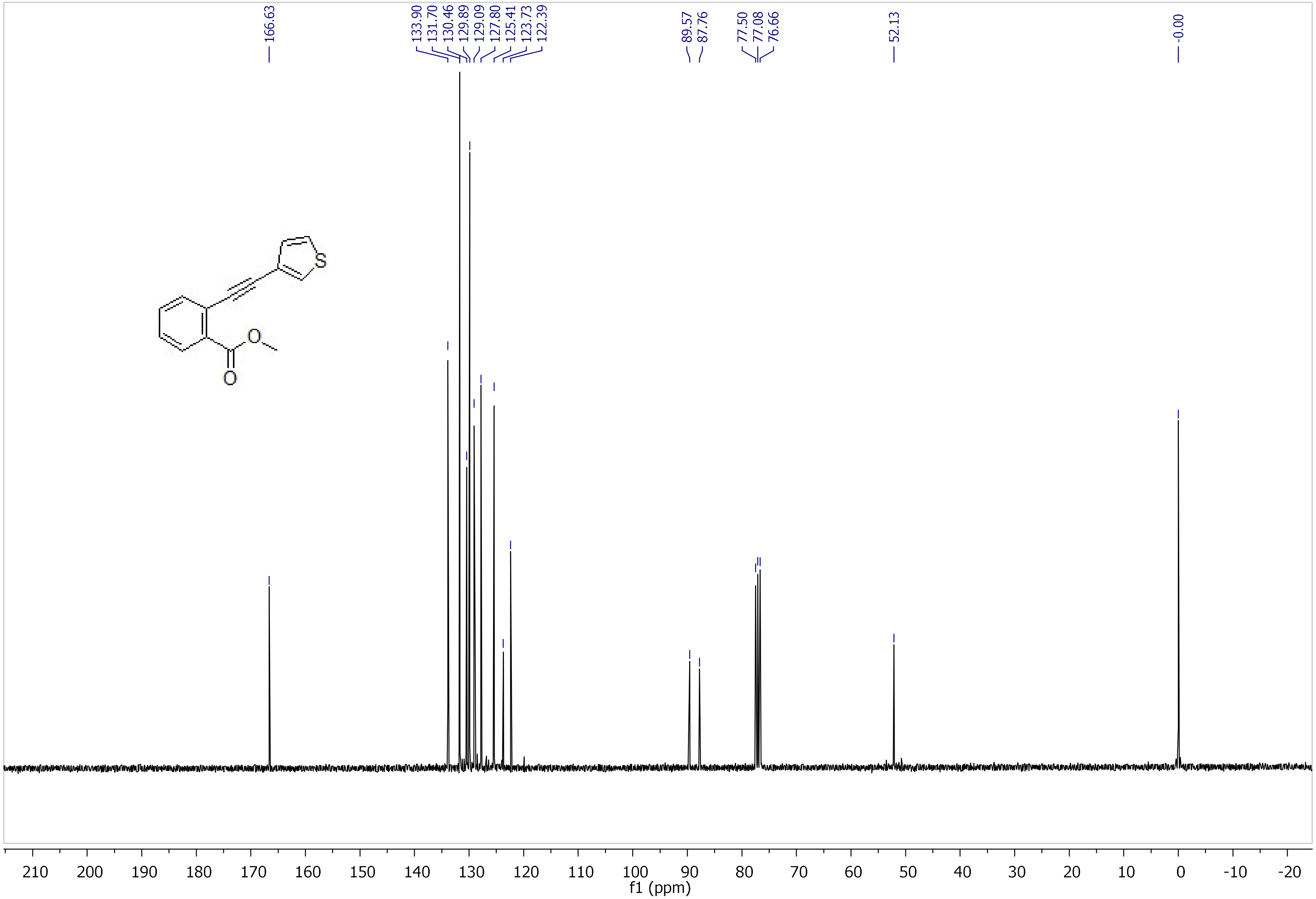
^{13}C NMR(CDCl$_3$)



Methyl 2-[2-(thiophen-3-yl)ethynyl]benzoate

^{1}H NMR(CDCl$_3$)

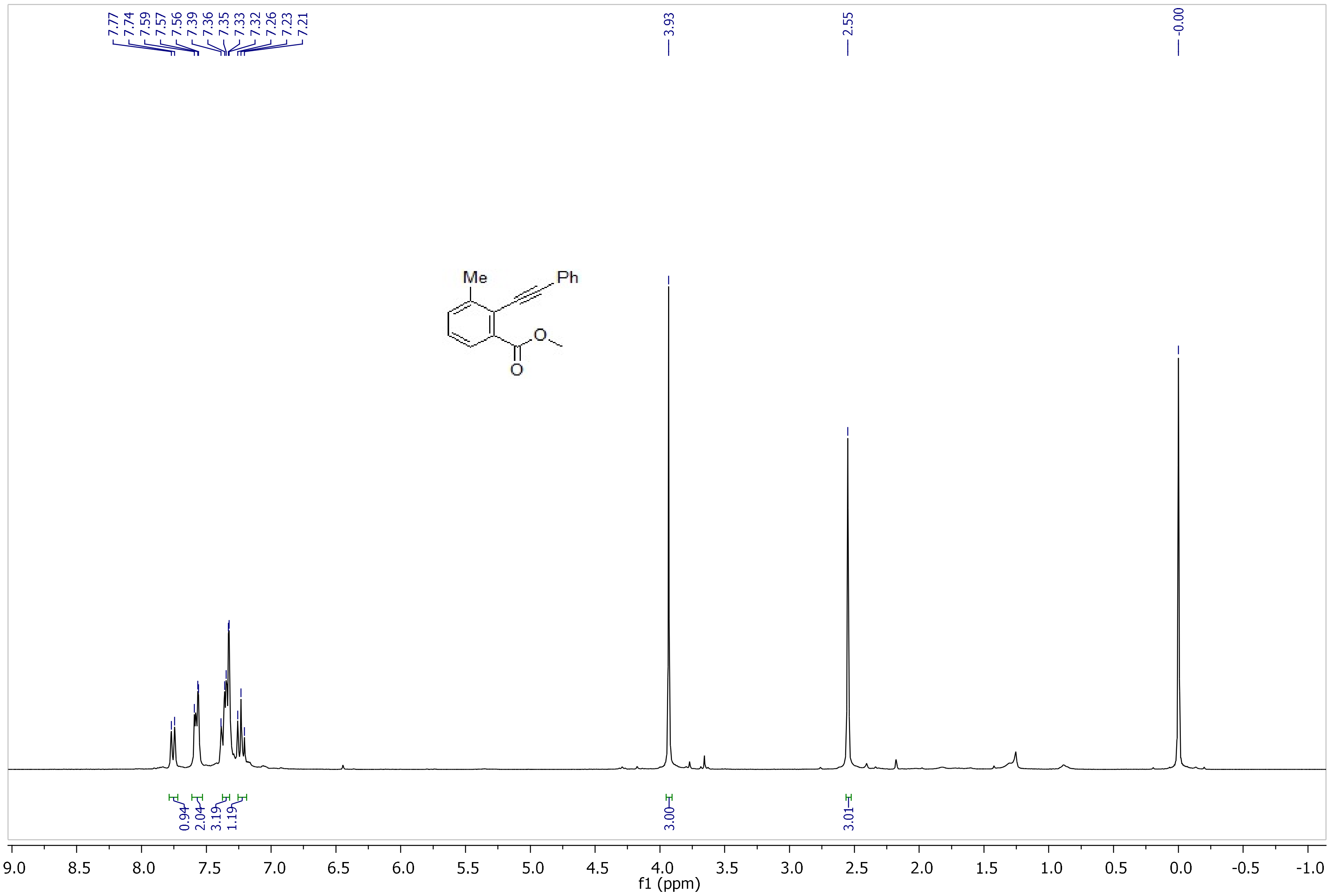




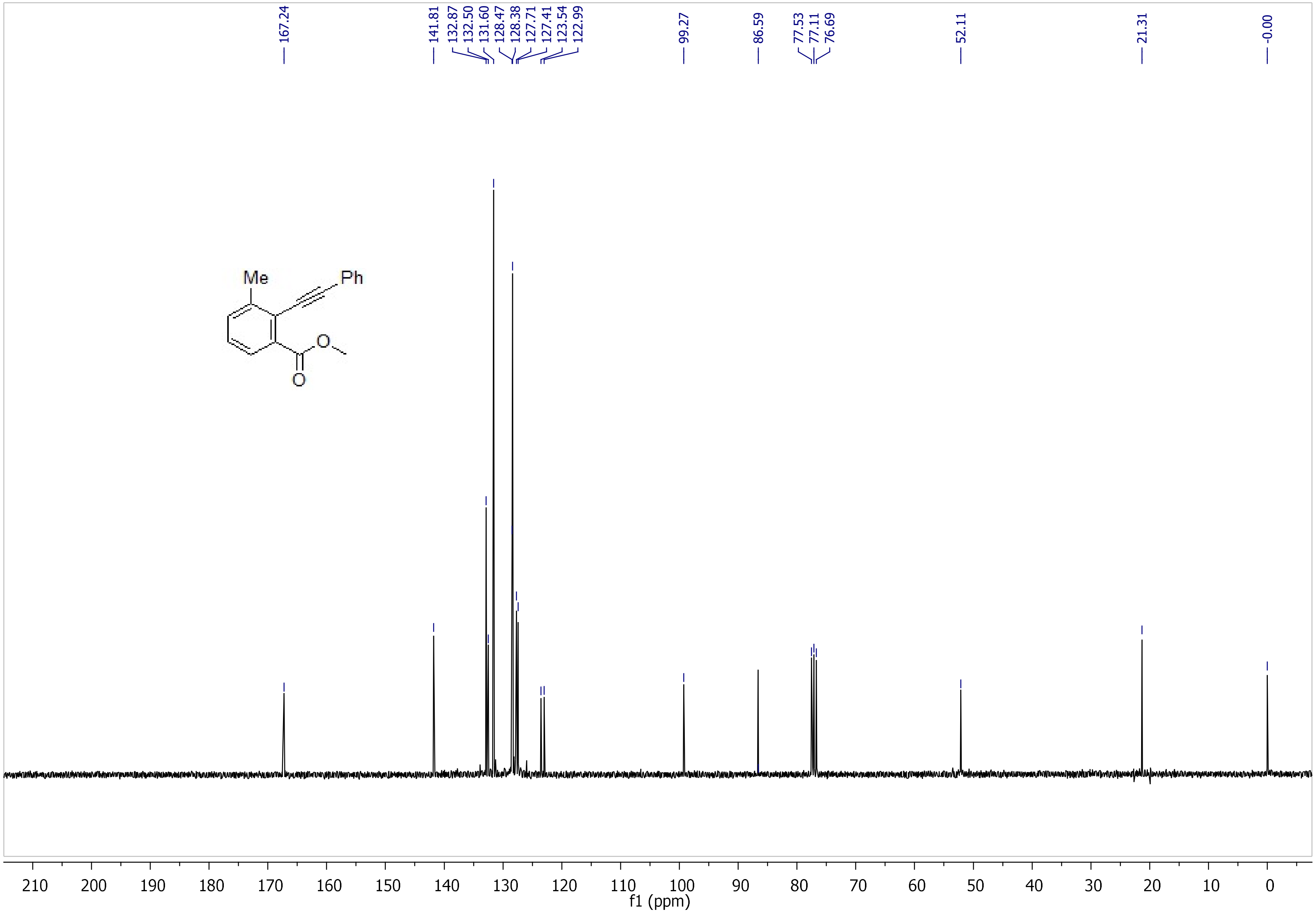
^{13}C NMR(CDCl$_3$)

Methyl 3-methyl-2-(2-phenylethynyl)benzoate

^{1}H NMR(CDCl$_3$)

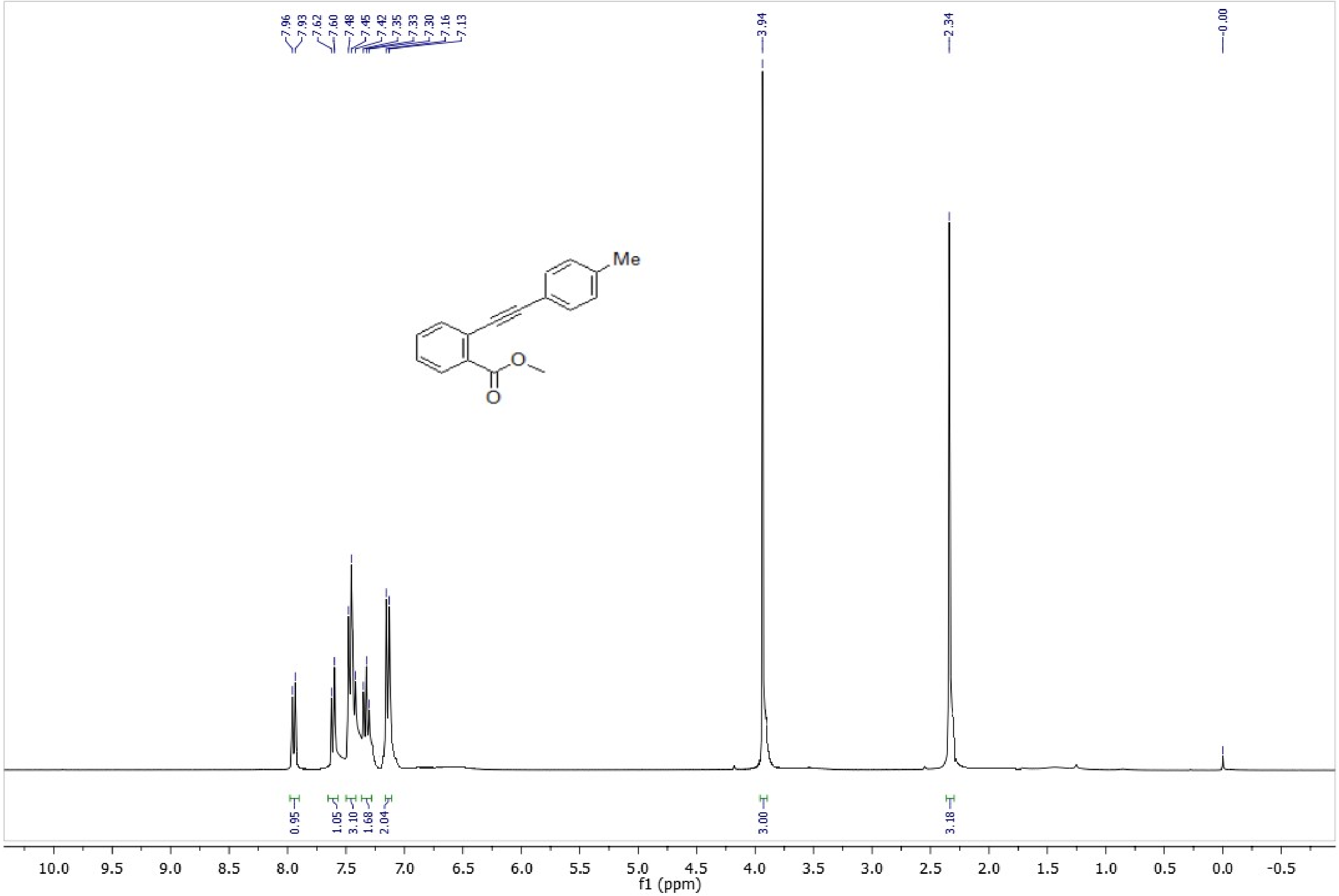


^{13}C NMR(CDCl$_3$)

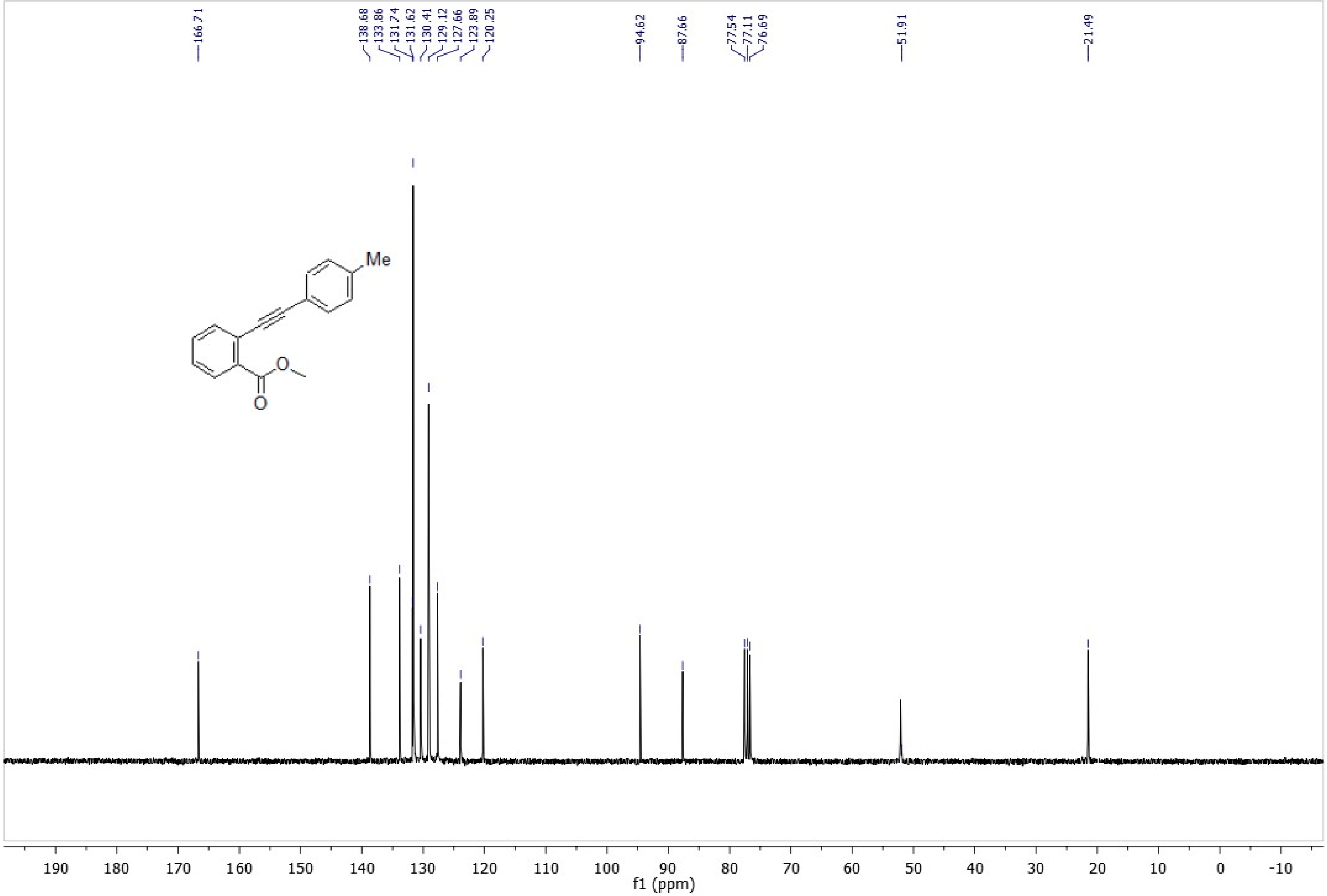


Methyl 2-(2-p-tolylethynyl)benzoate

^{1}H NMR(CDCl$_3$)

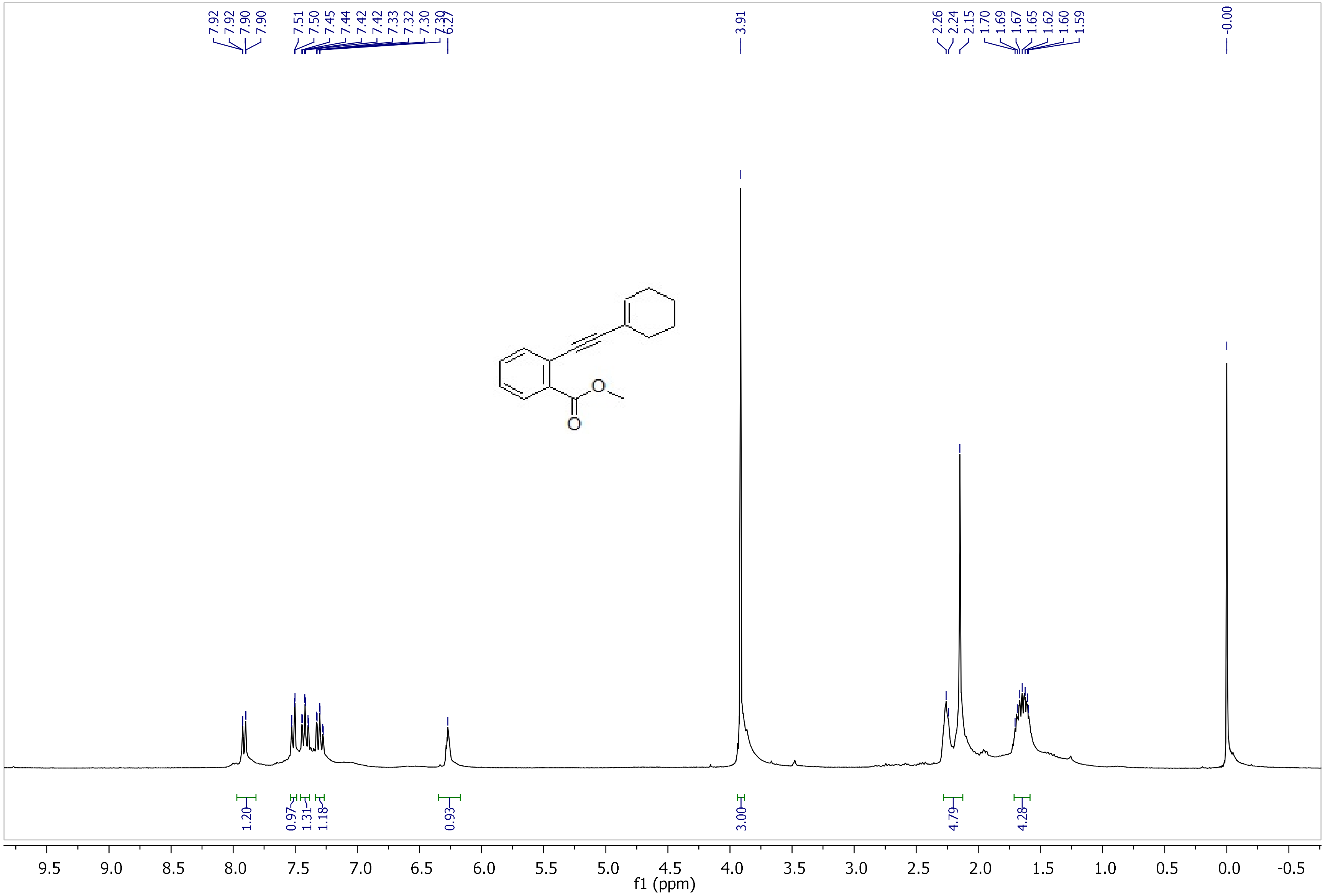


^{13}C NMR(CDCl$_3$)

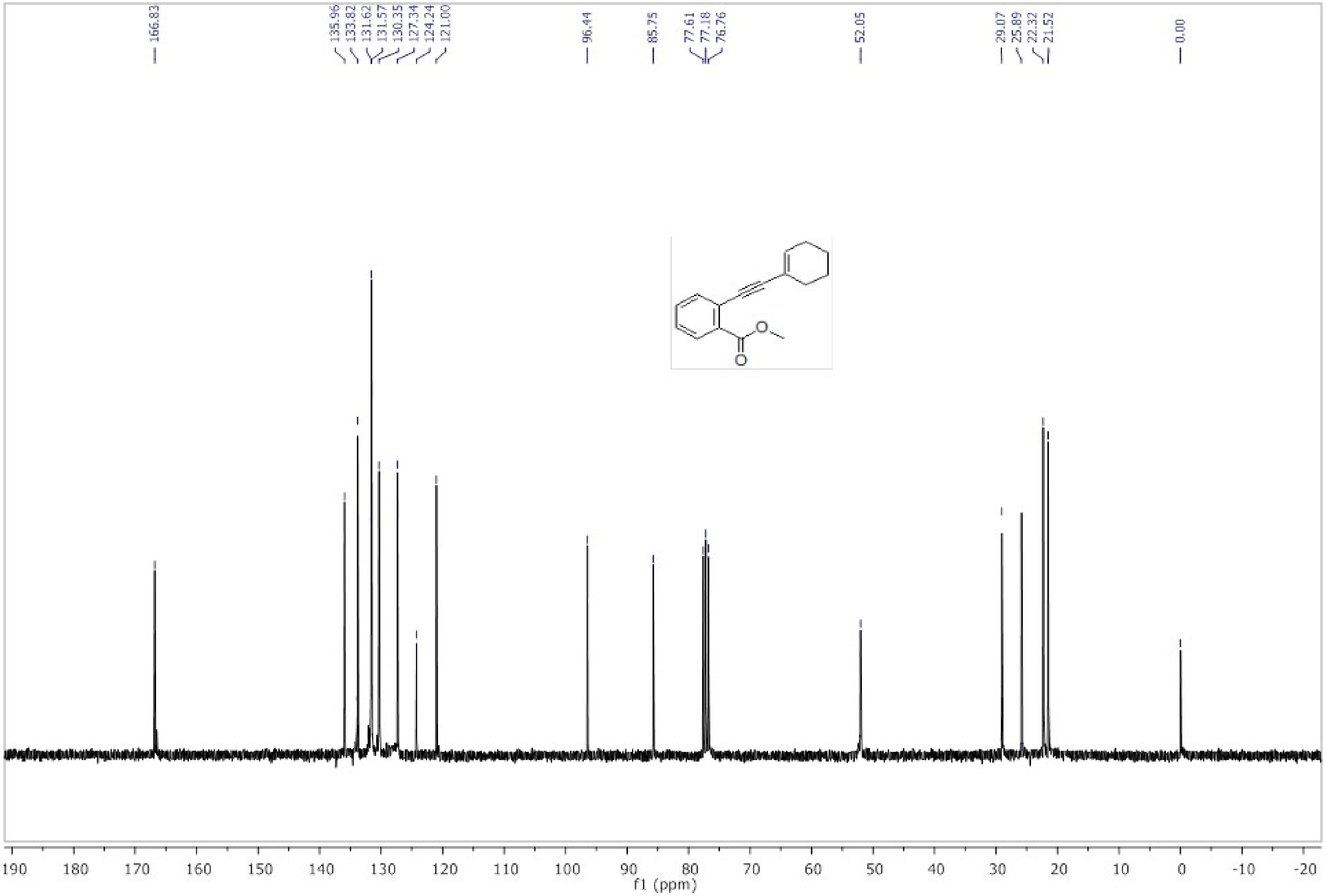


Methyl 2-(2-cyclohexenylethynyl)benzoate

^{1}H NMR(CDCl$_3$)

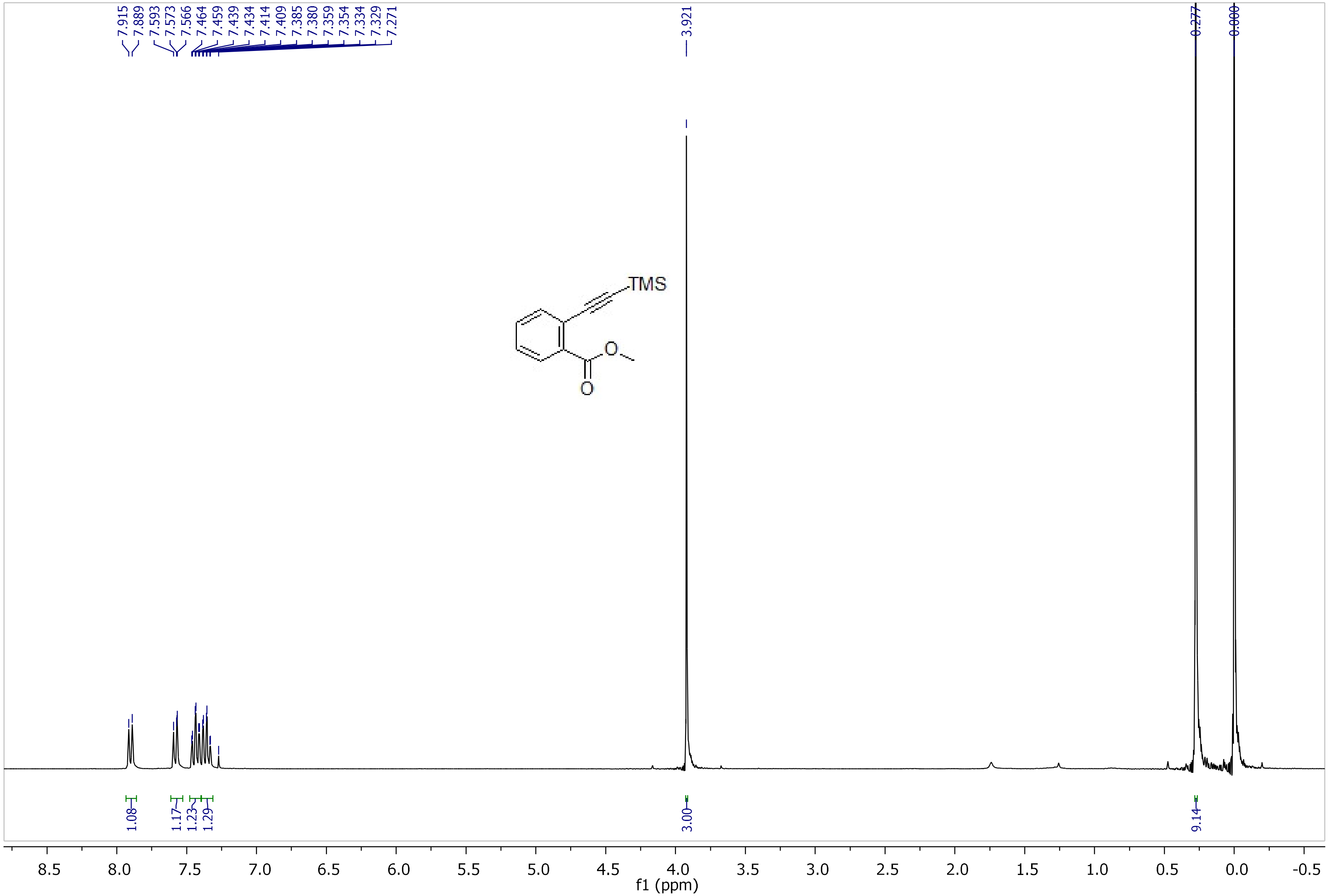


^{13}C NMR(CDCl$_3$)

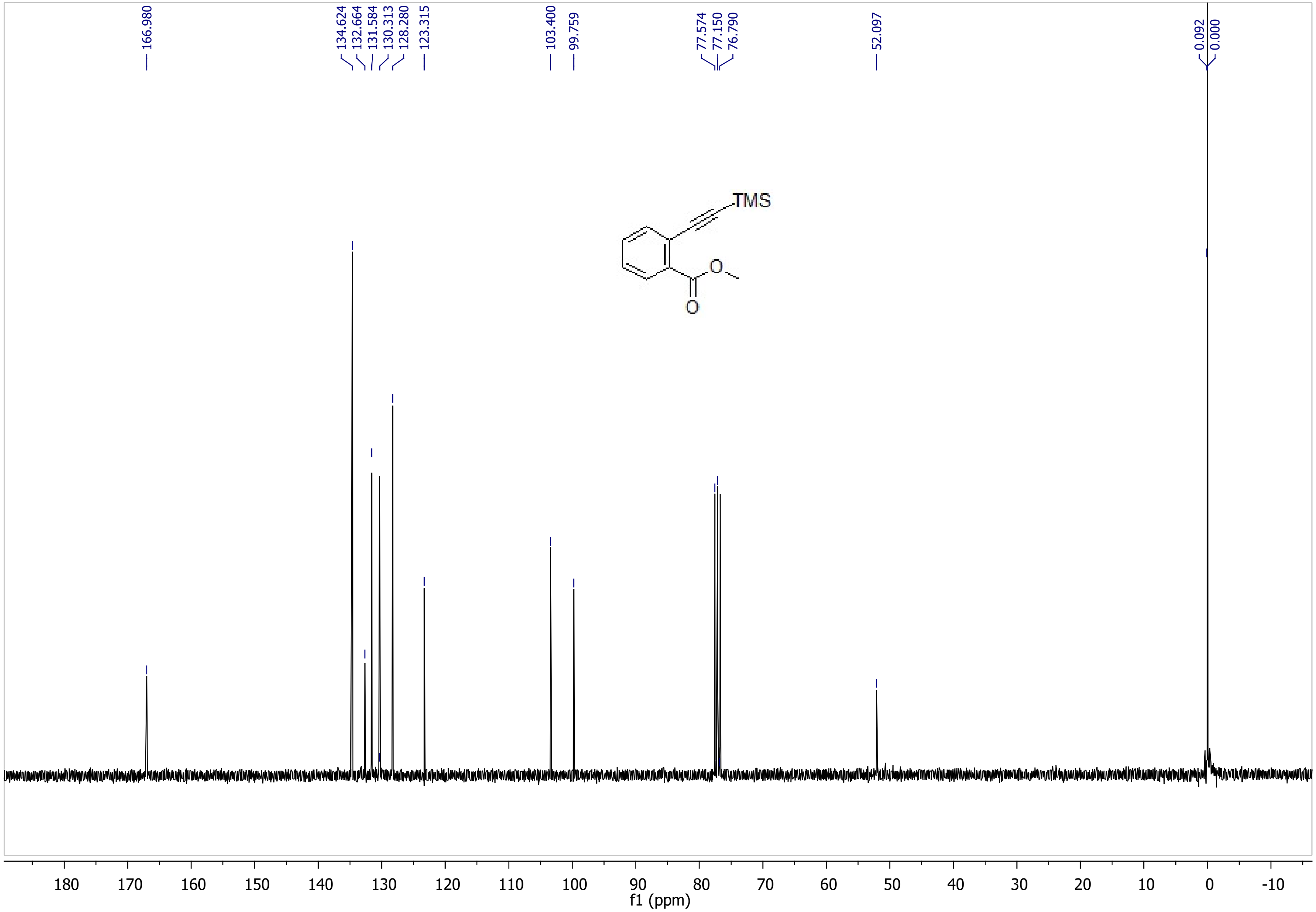


Methyl 2-[2-(trimethylsilyl)ethynyl]benzoate

^{1}H NMR(CDCl$_3$)

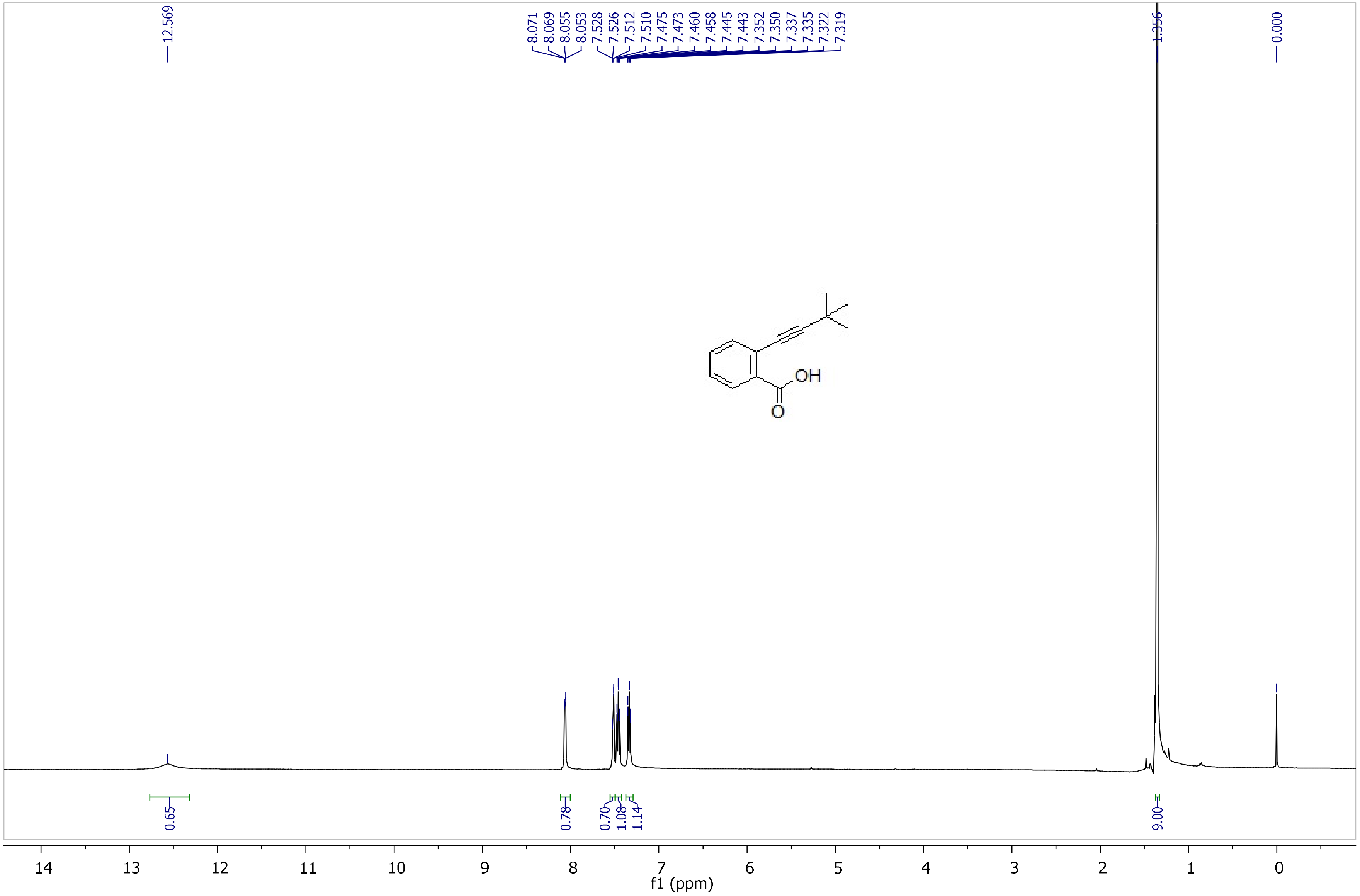


^{13}C NMR(CDCl$_3$)

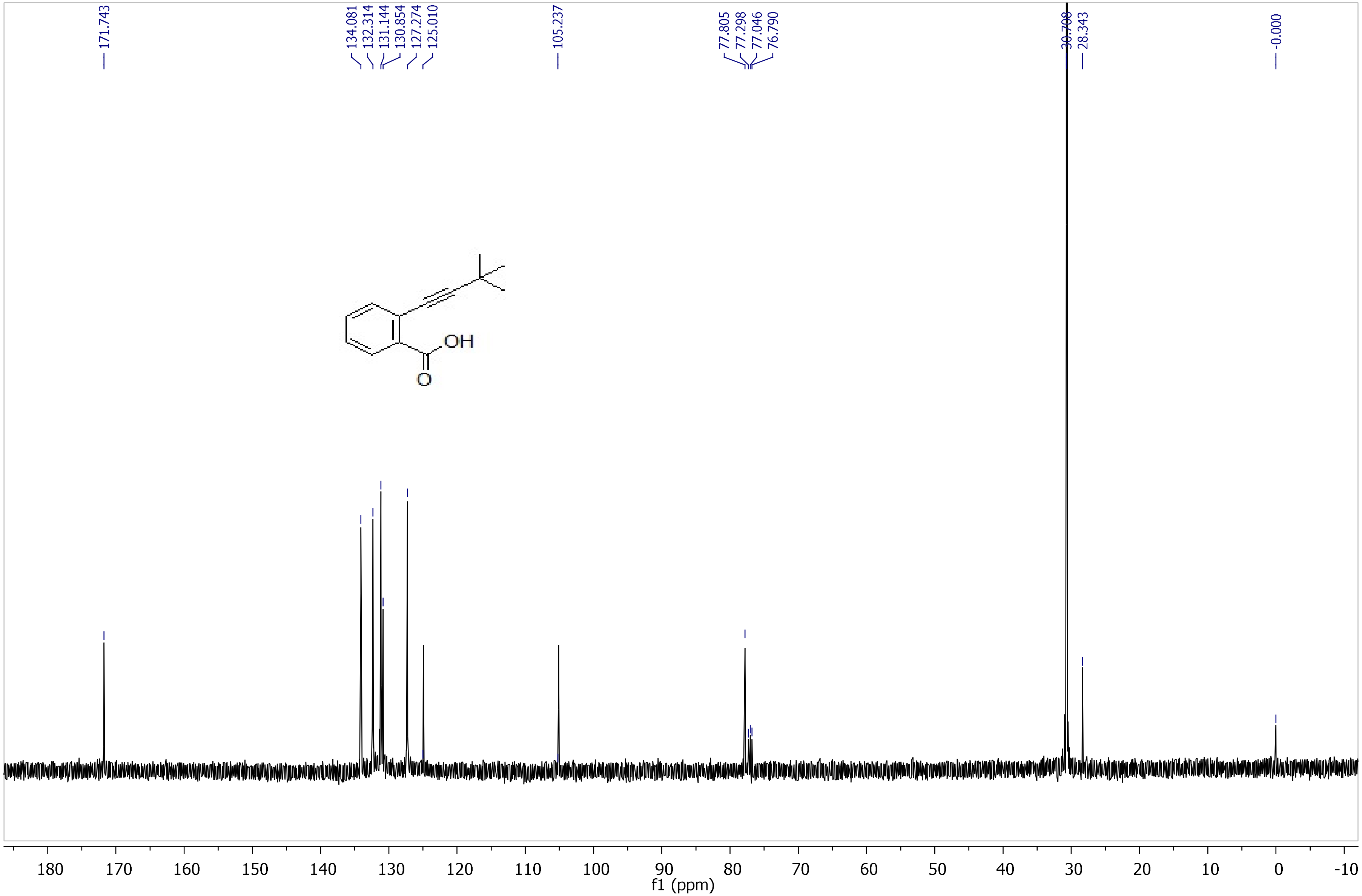


2-(3,3-Dimethylbut-1-ynyl)benzoic acid (**1a**)

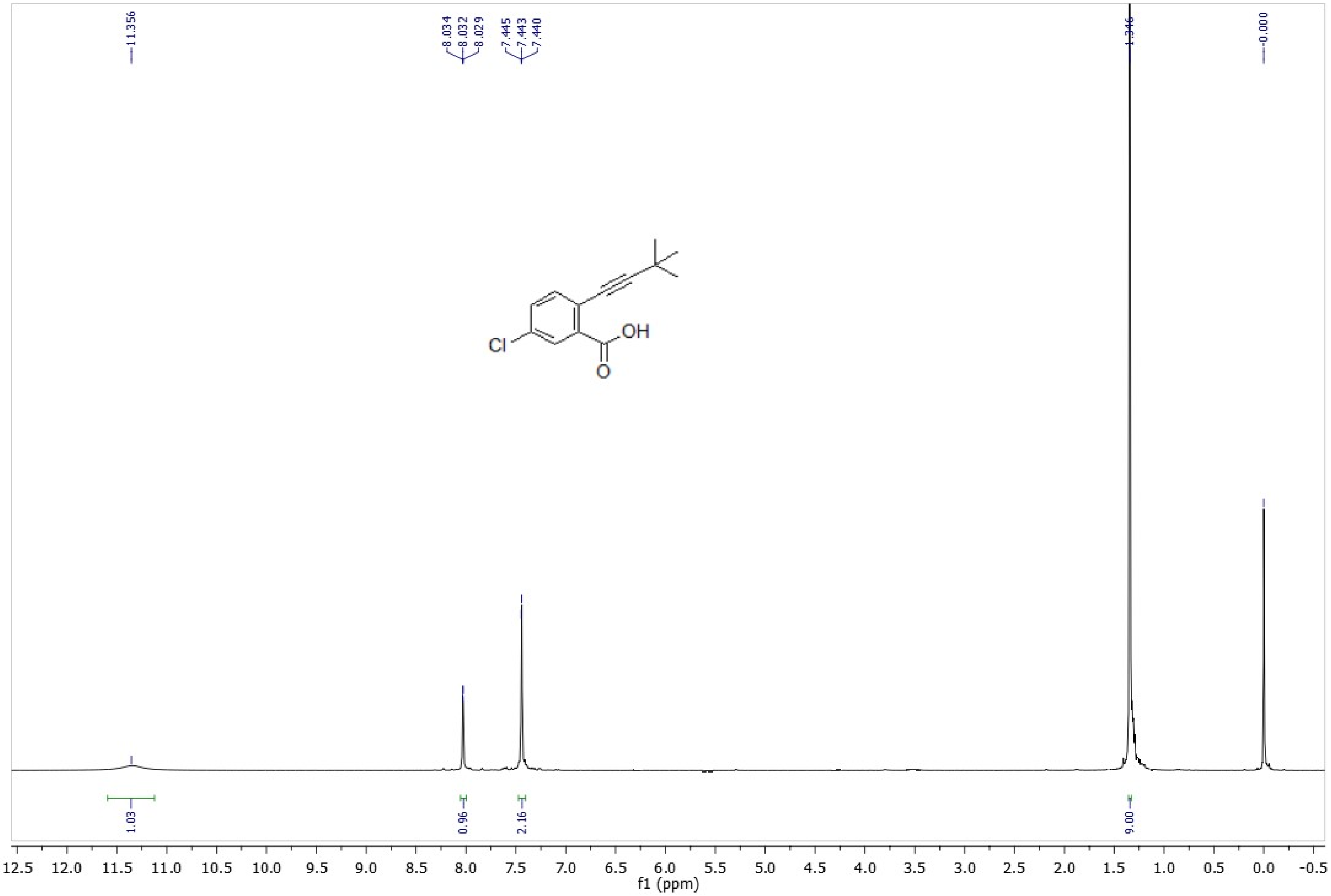
^{1}H NMR(CDCl$_3$)



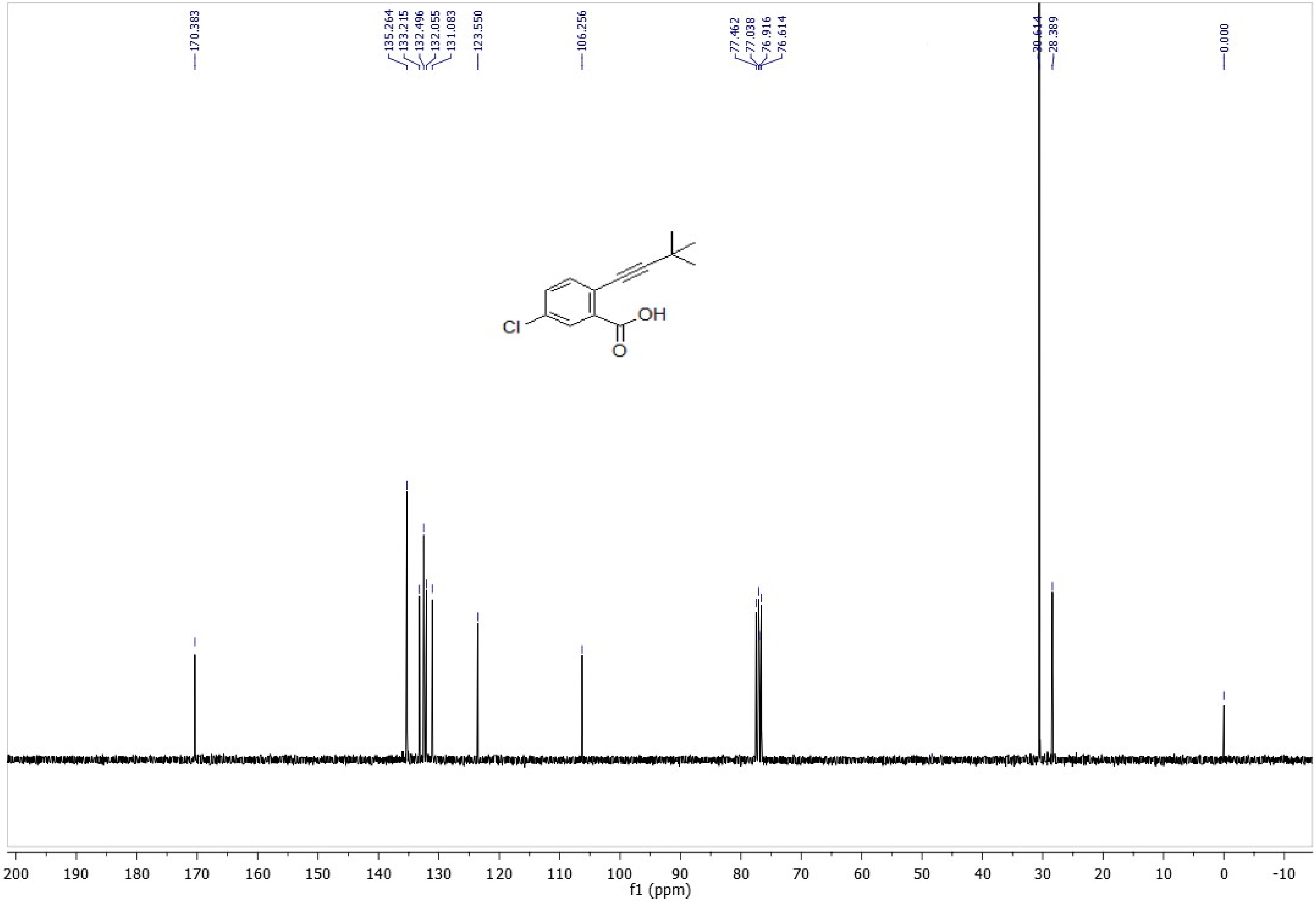
^{13}C NMR(CDCl$_3$)



5-Chloro-2-(3,3-dimethylbut-1-ynyl)benzoic acid (**1b**)
^{1}H NMR(CDCl$_3$)

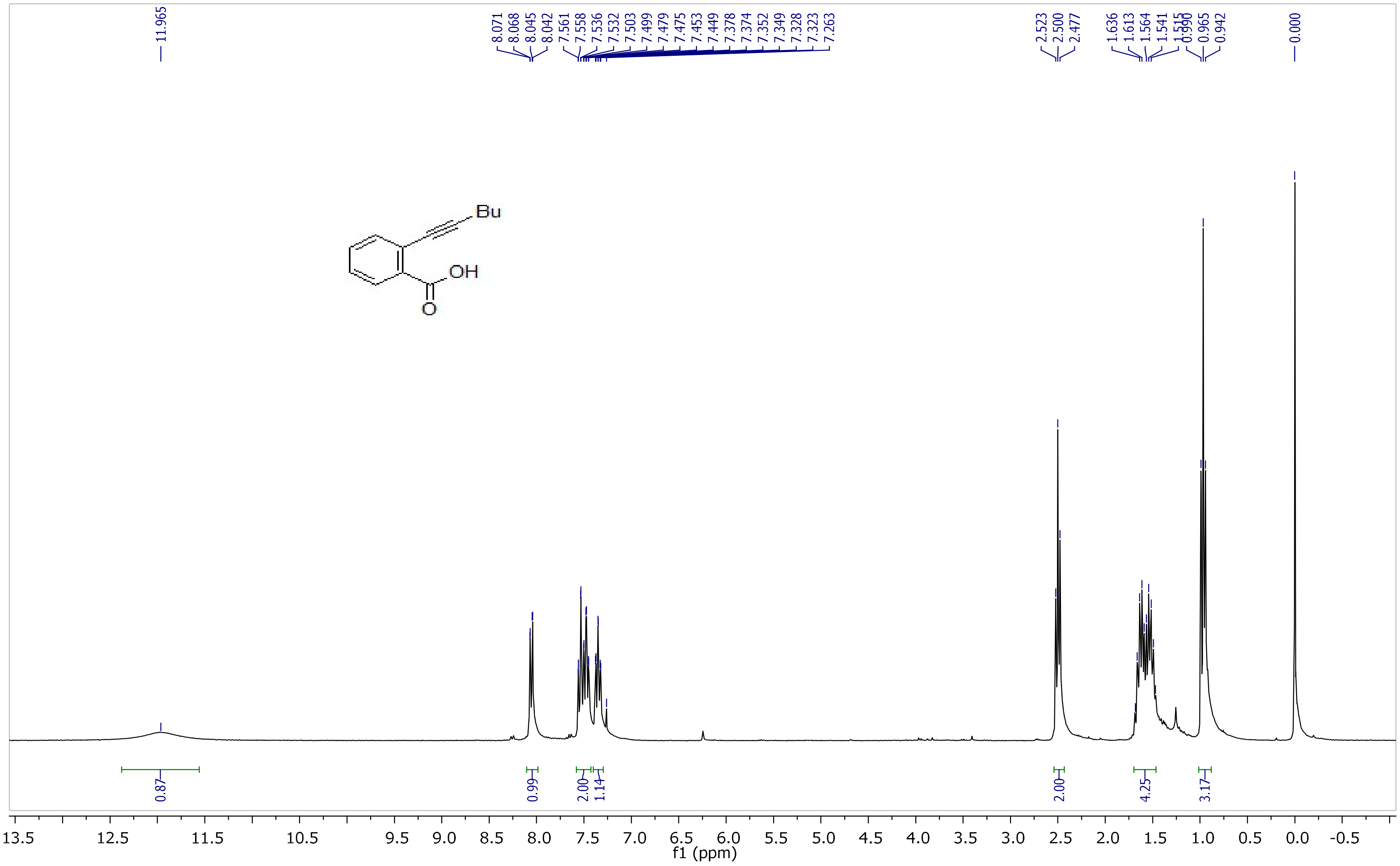


^{13}C NMR(CDCl$_3$)

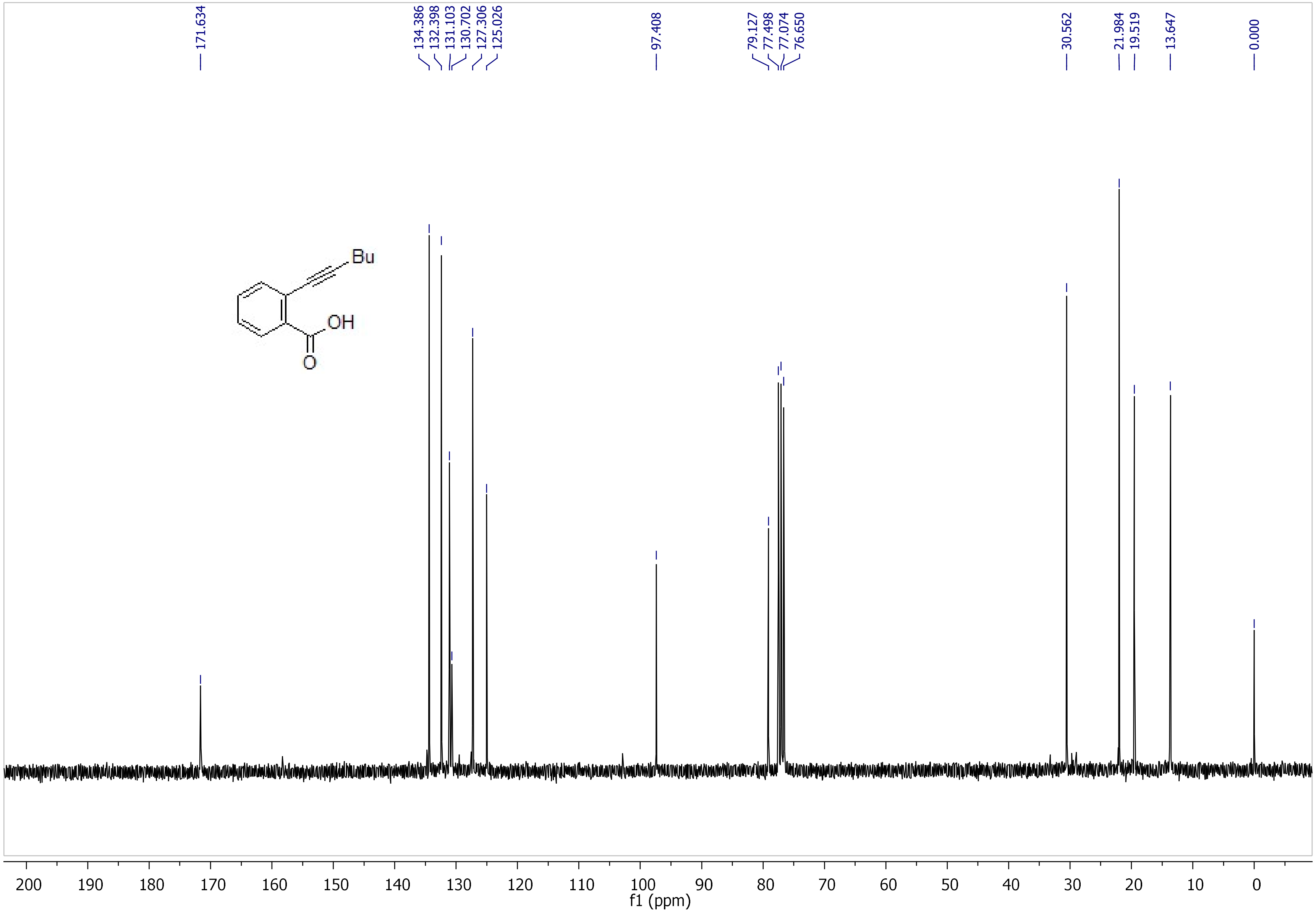


2-(Hex-1-ynyl)benzoic acid (**1c**)

^{1}H NMR(CDCl$_3$)

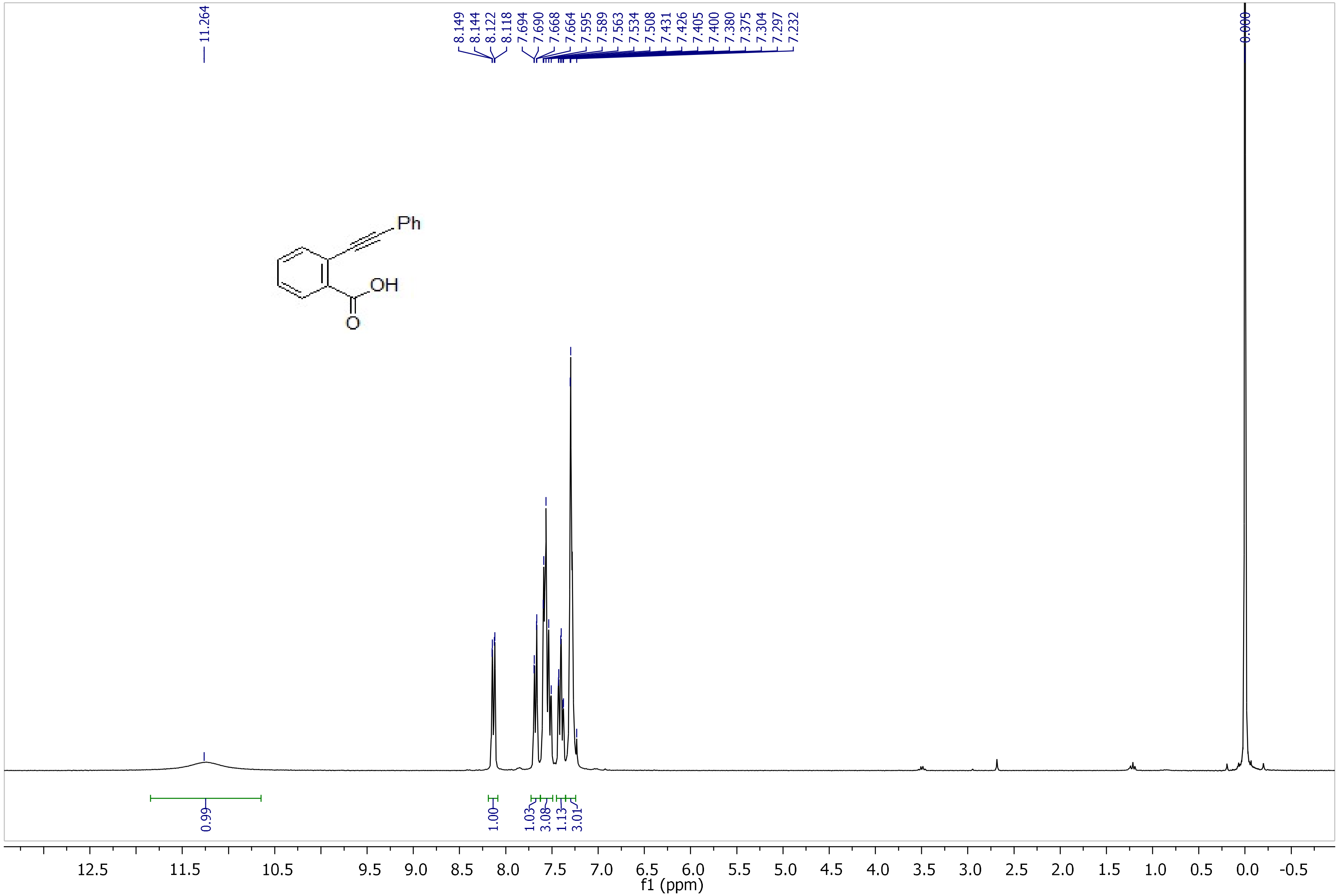


^{13}C NMR(CDCl$_3$)

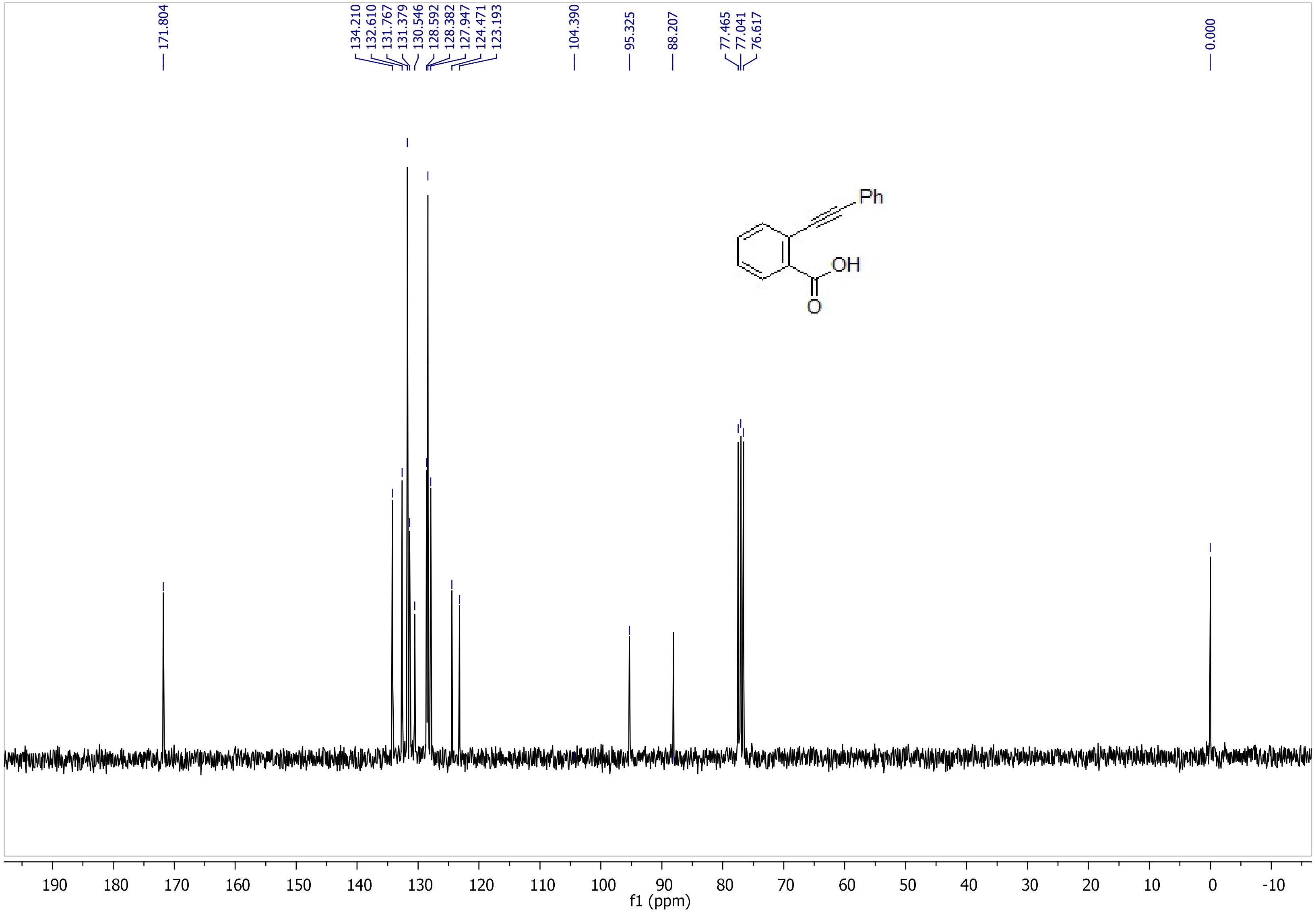


2-(2-Phenylethynyl)benzoic acid (1d)

^{1}H NMR(CDCl$_3$)

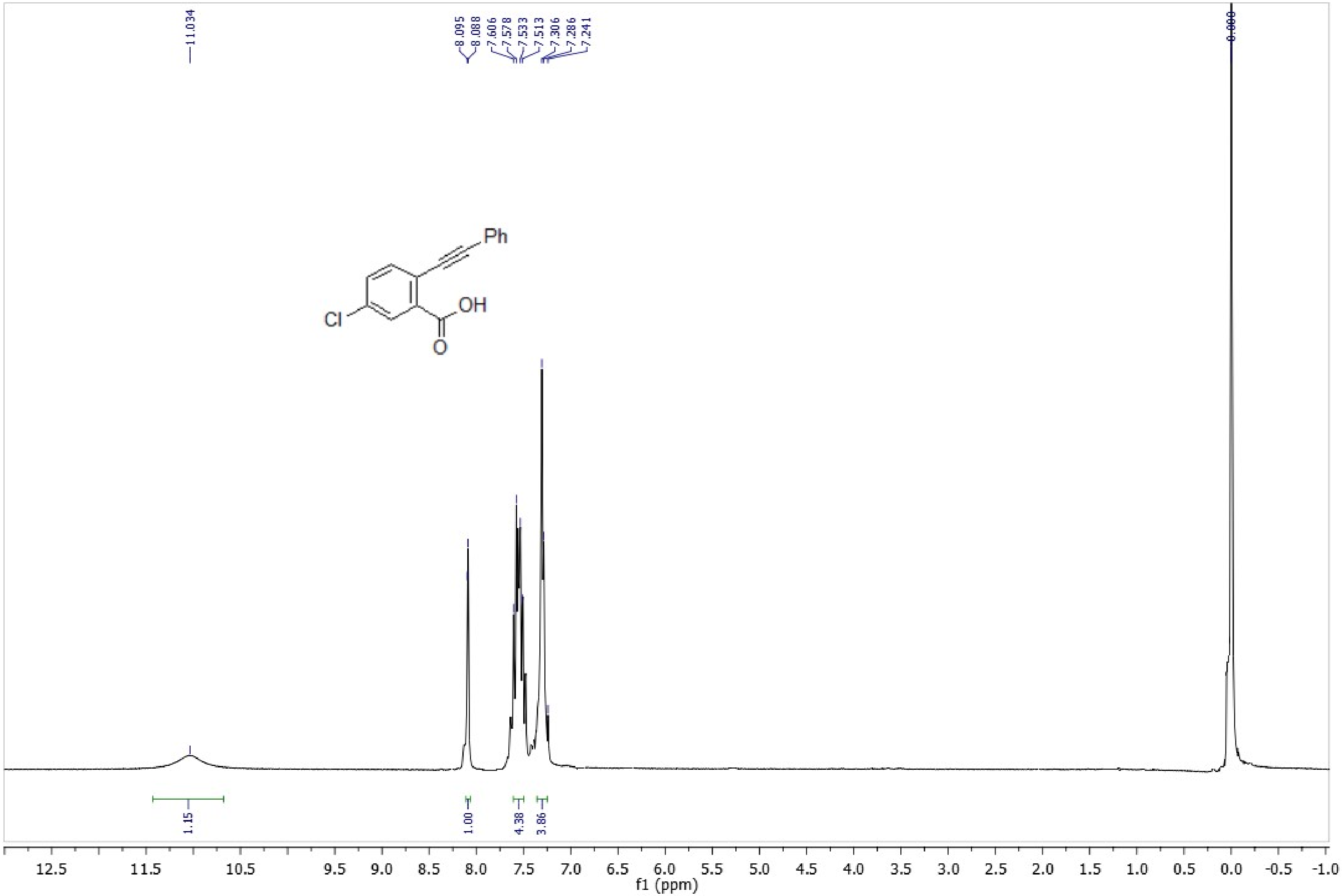


^{13}C NMR(CDCl$_3$)

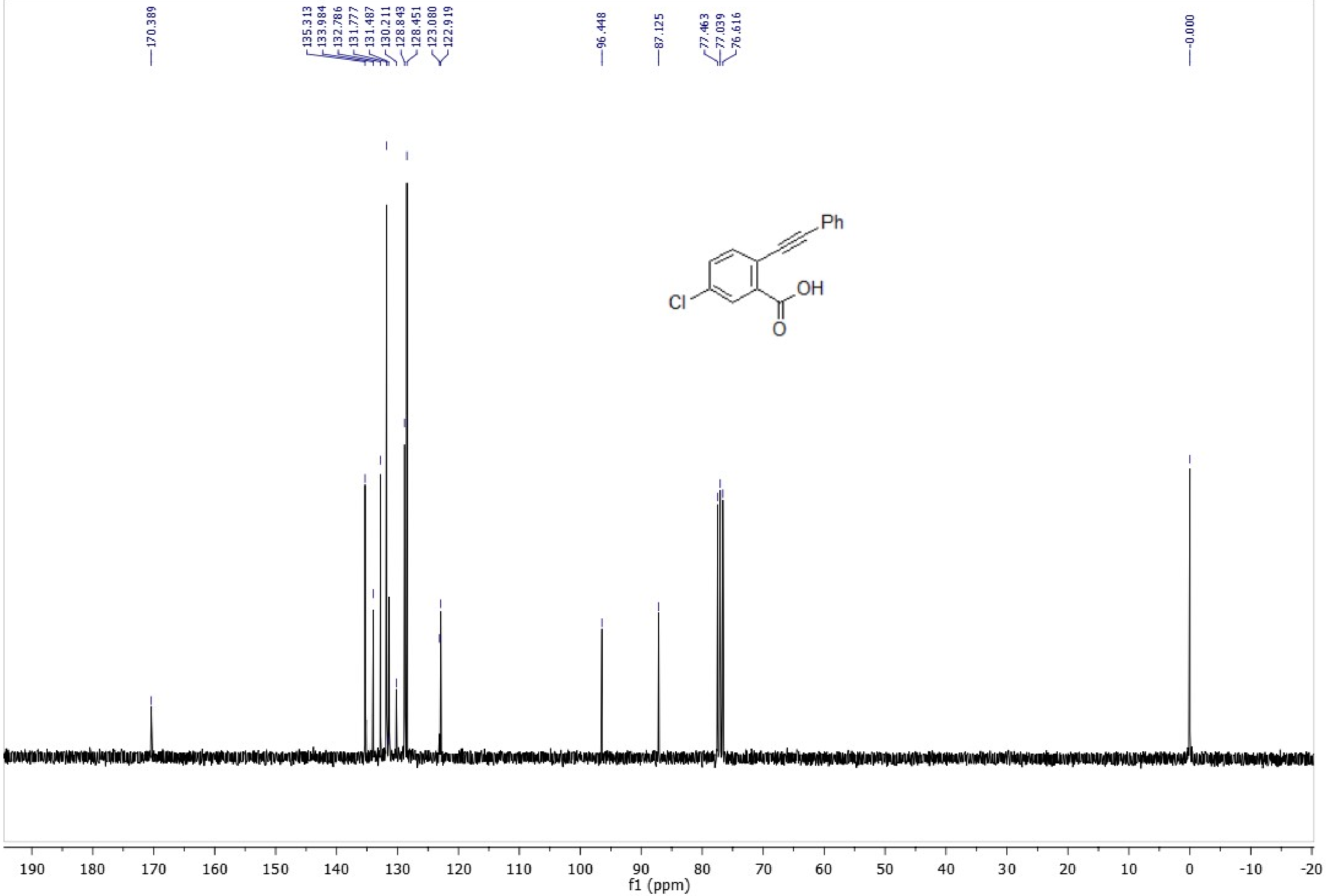


5-Chloro-2-(2-phenylethynyl)benzoic acid (**1e**)

^{1}H NMR($CDCl_3$)

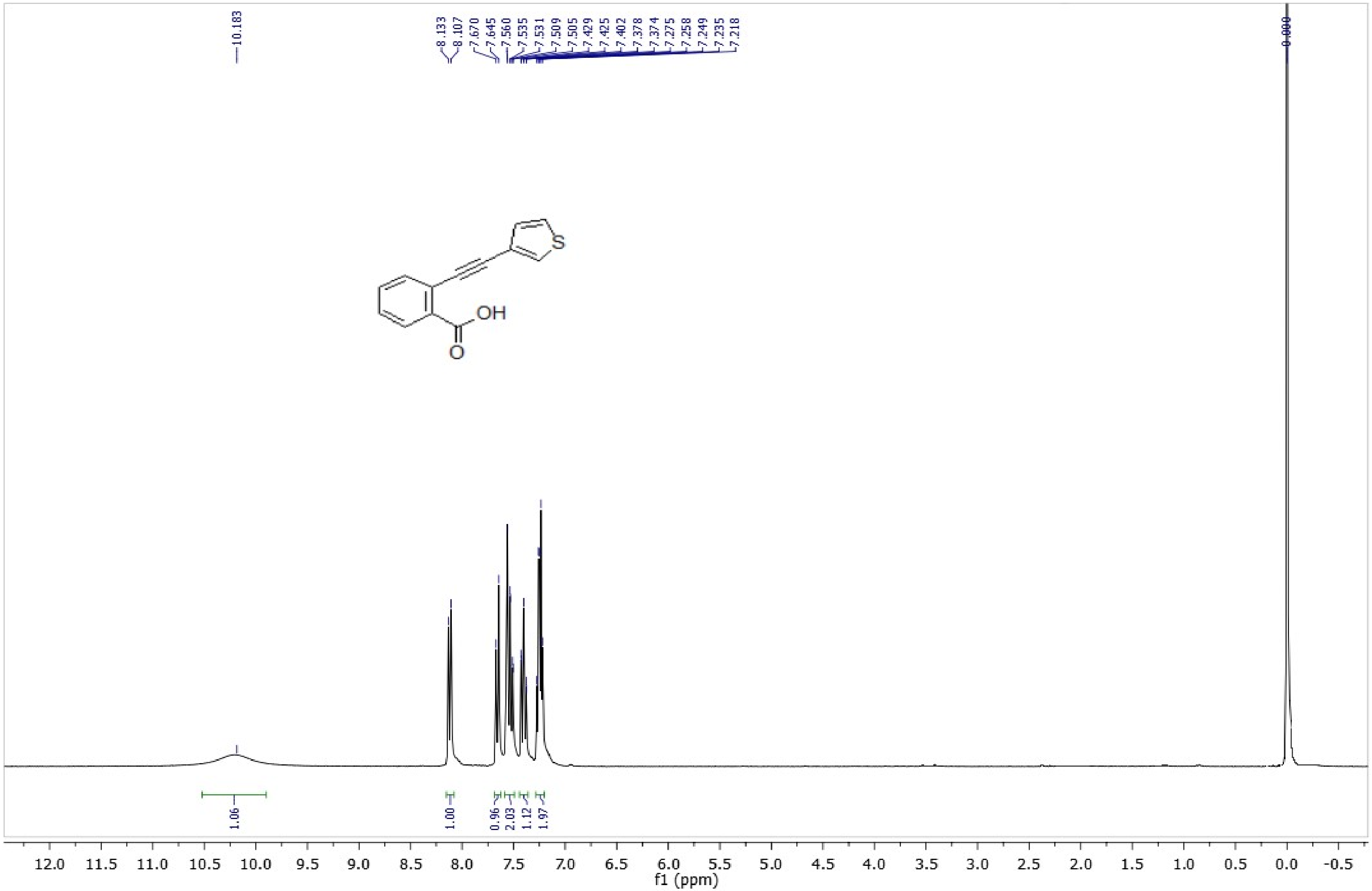


^{13}C NMR(CDCl$_3$)

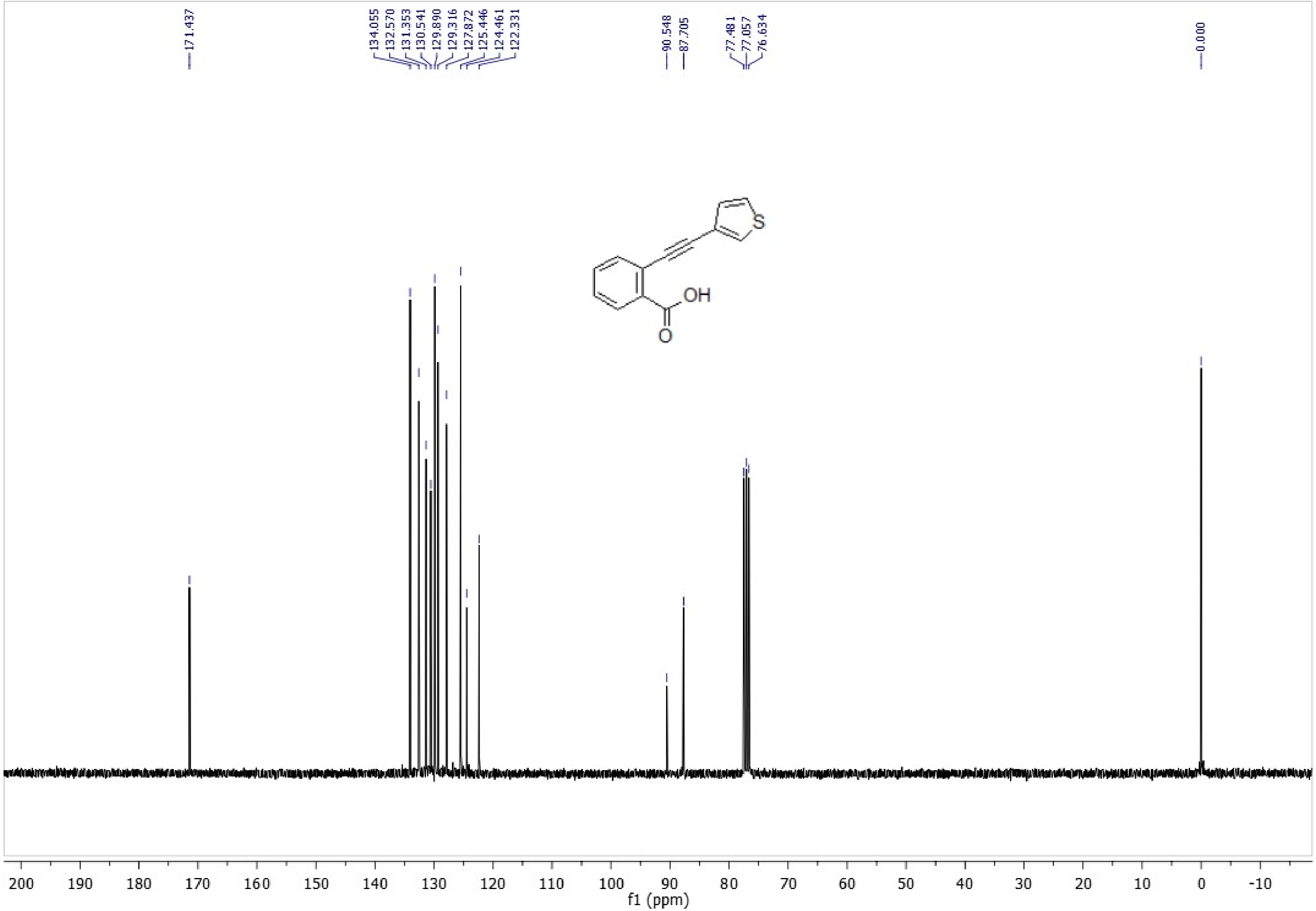


2-(2-Thiophen-3-yl)ethynyl]benzoic acid (**1f**)

^{1}H NMR($CDCl_3$)



^{13}C NMR($CDCl_3$)


171.437
134.055
132.570
131.353
130.541
129.890
129.316
127.872
125.446
124.461
122.331
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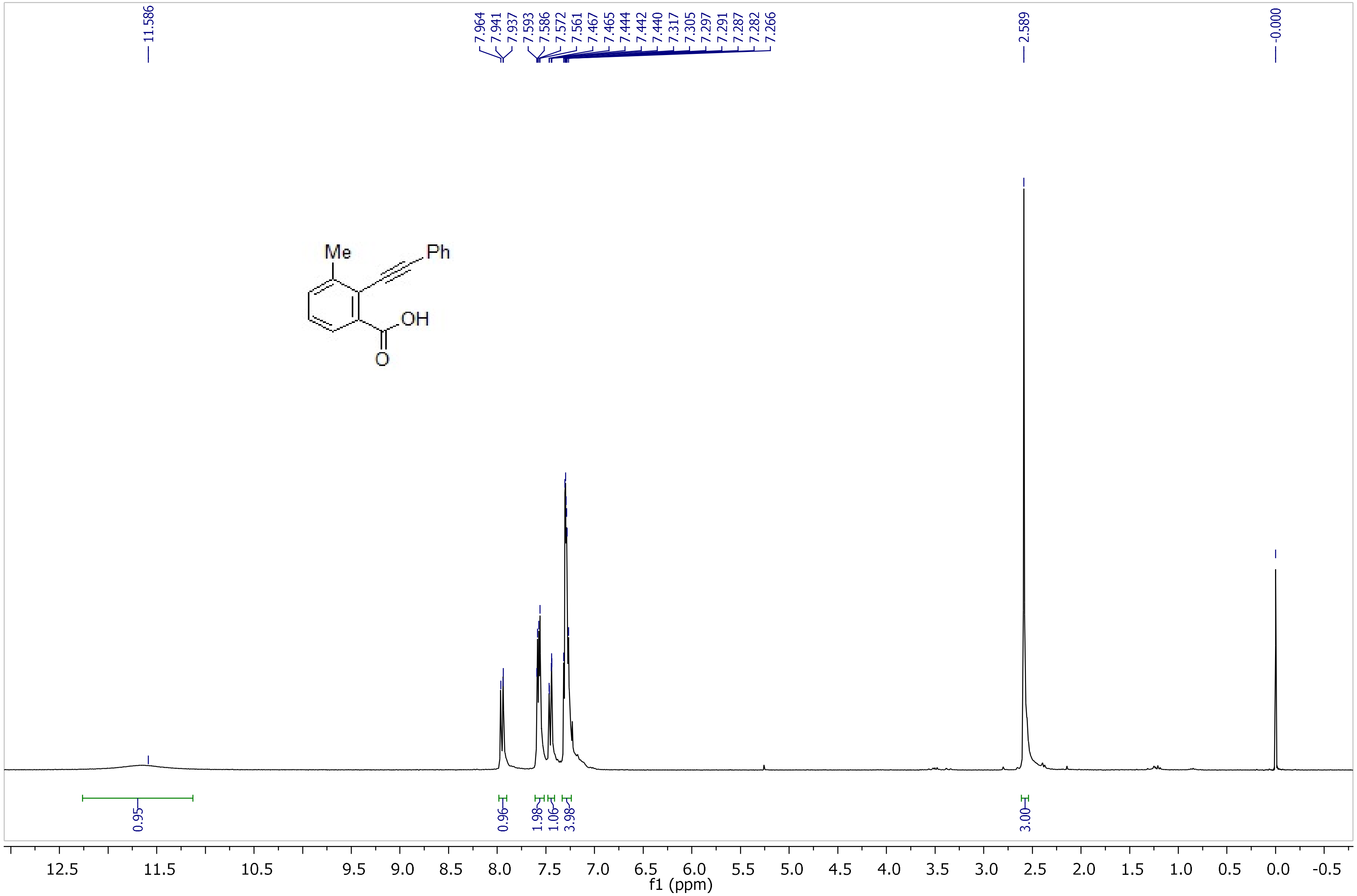
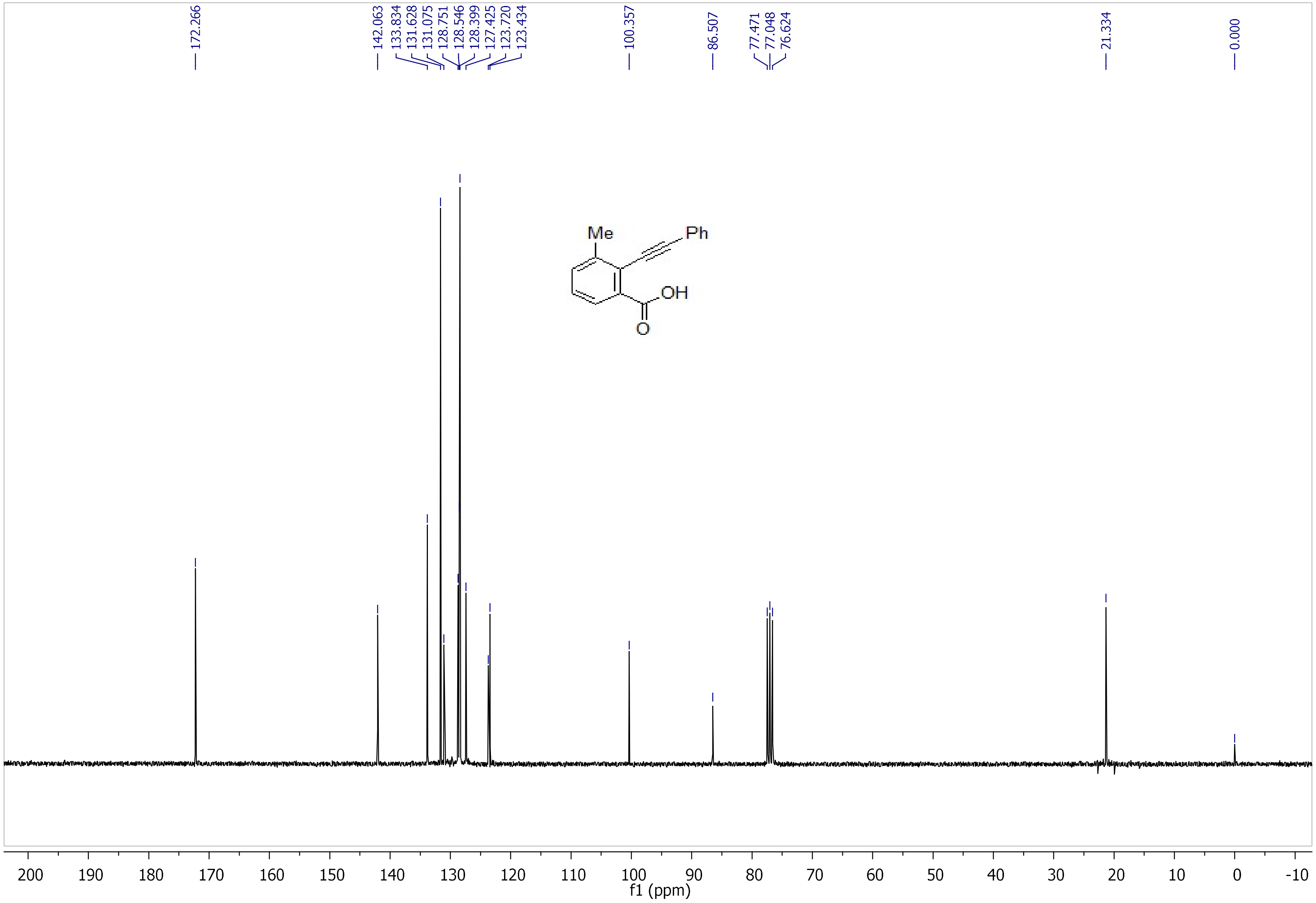
87.705
77.481
77.057
76.634
0.000
S
OH
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3-Methyl-2-(2-phenylethynyl)benzoic acid (1g)

^{1}H NMR(CDCl$_3$)

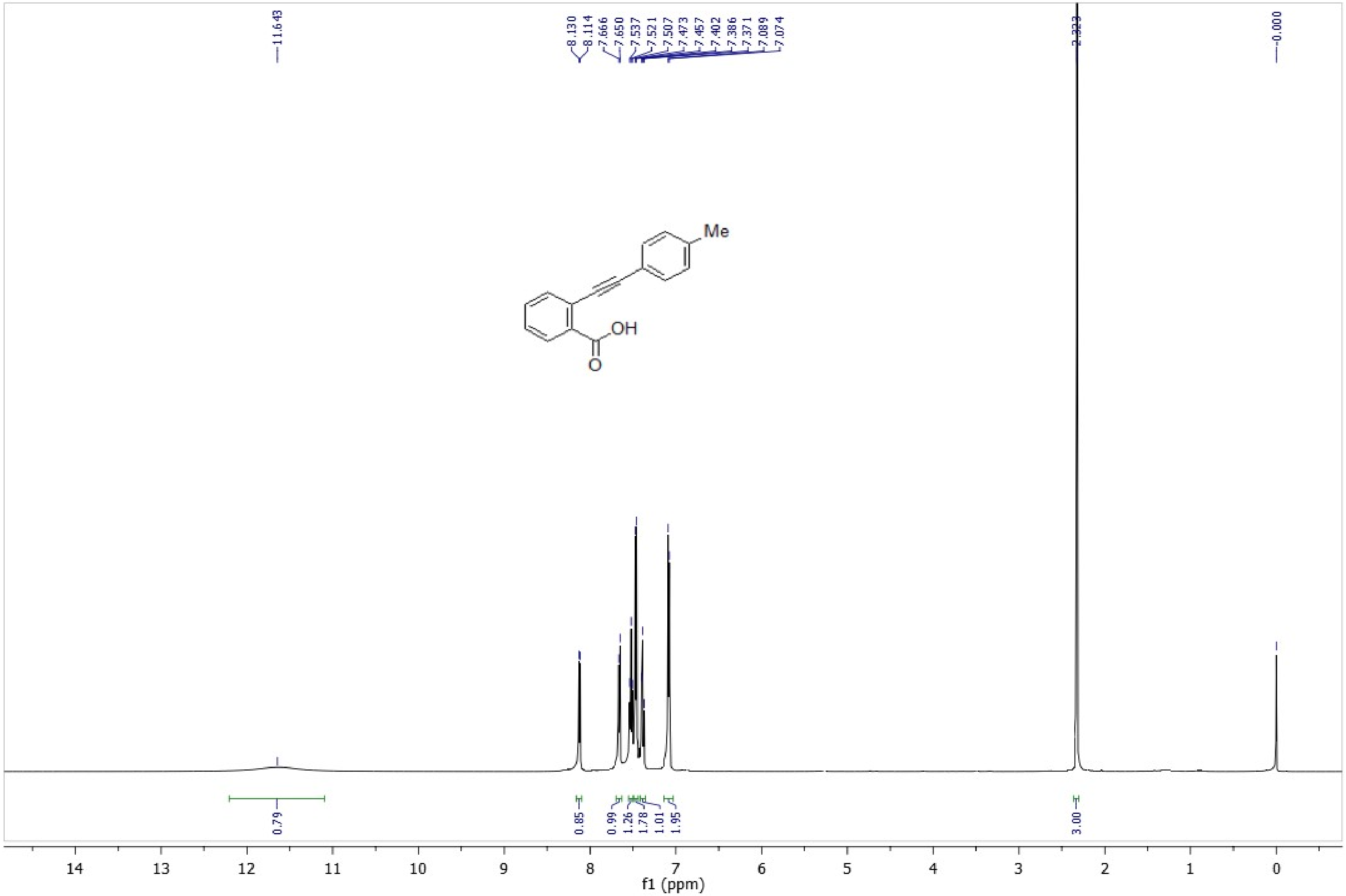


^{13}C NMR(CDCl$_3$)

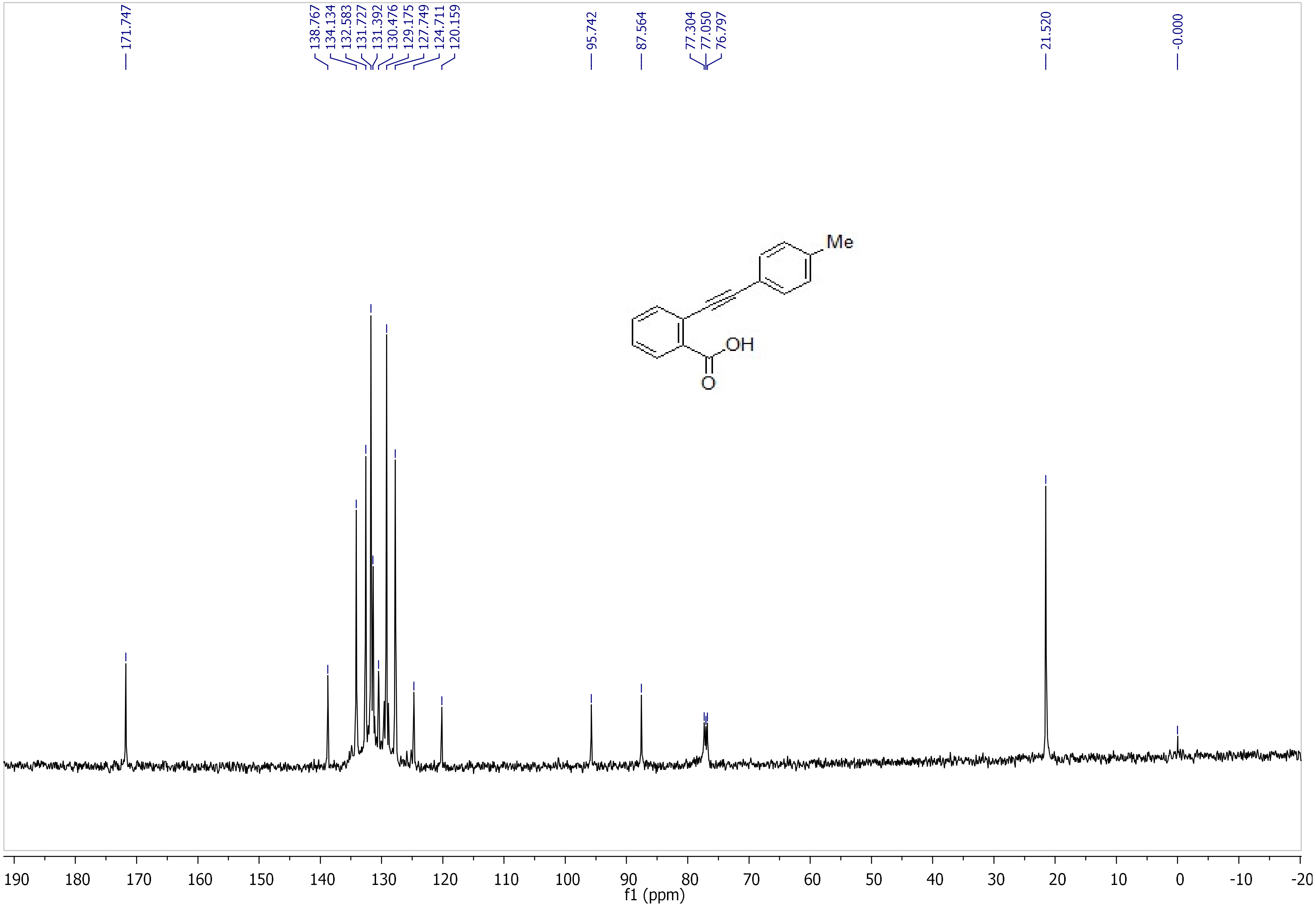


2-p-Tolylethynylbenzoic acid (**1h**)

^{1}H NMR(CDCl$_3$)

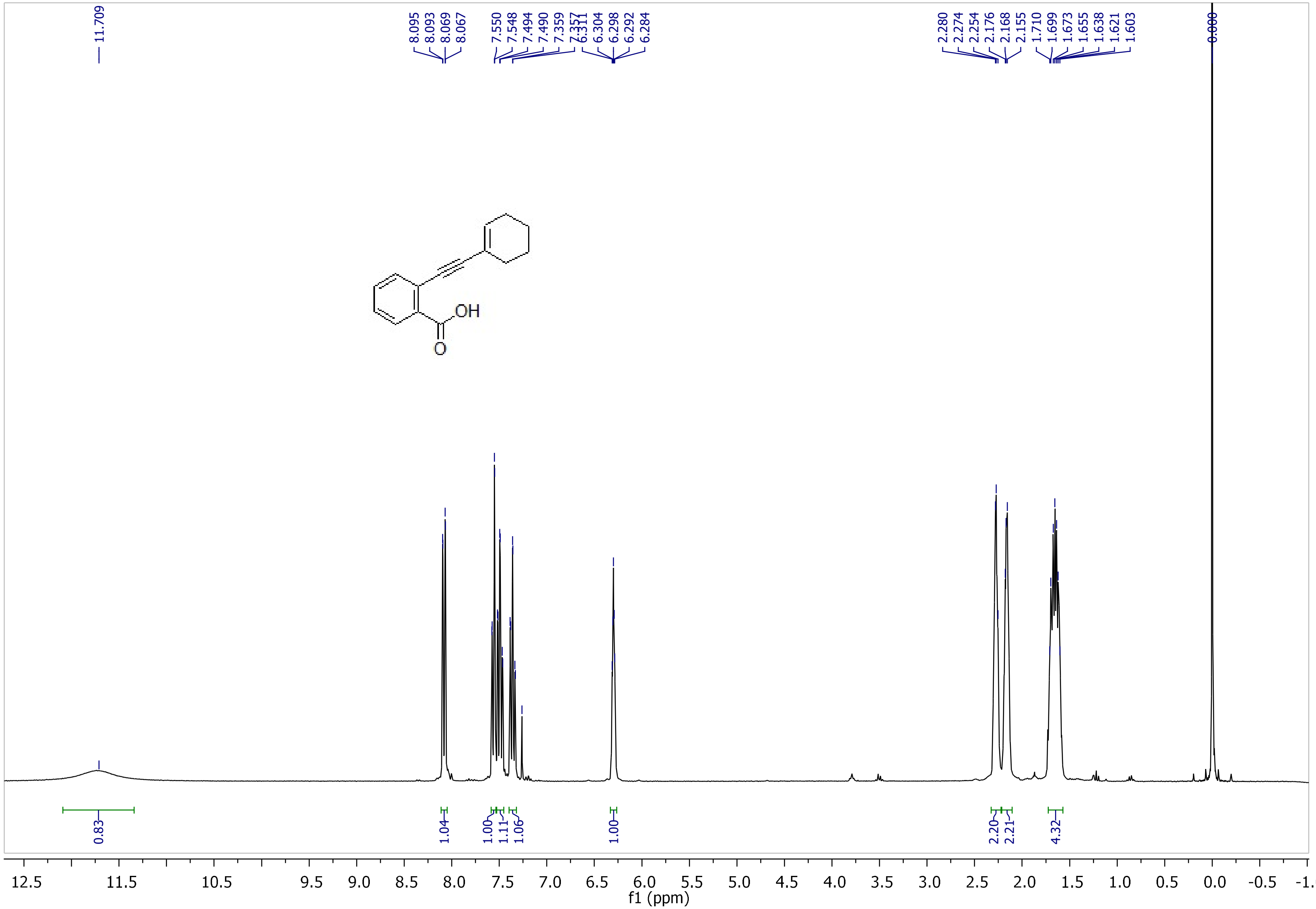


^{13}C NMR(CDCl$_3$)

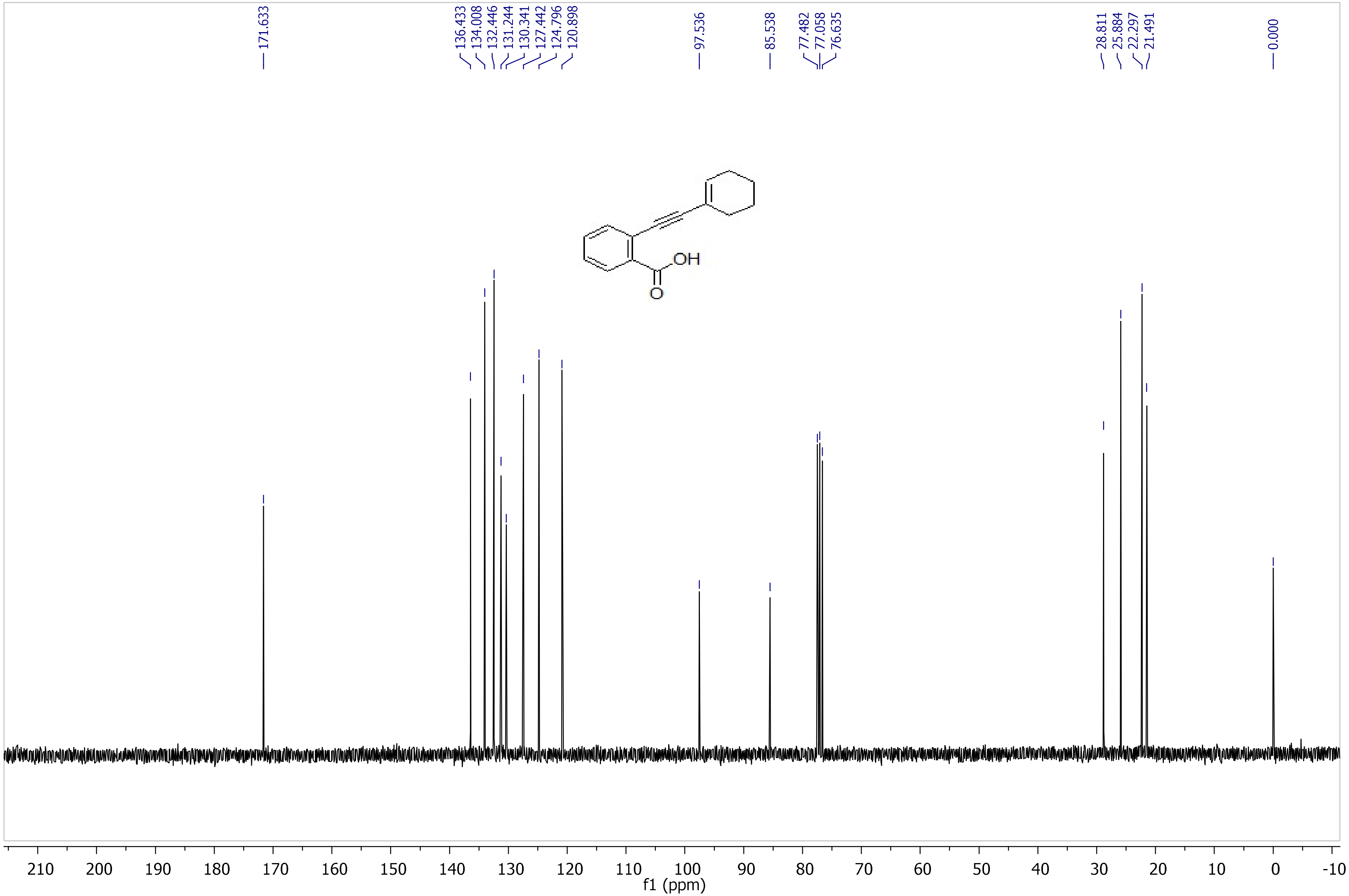


2-[(1-Cyclohexenyl)ethynyl]benzoic acid (**1i**)

^{1}H NMR(CDCl$_3$)

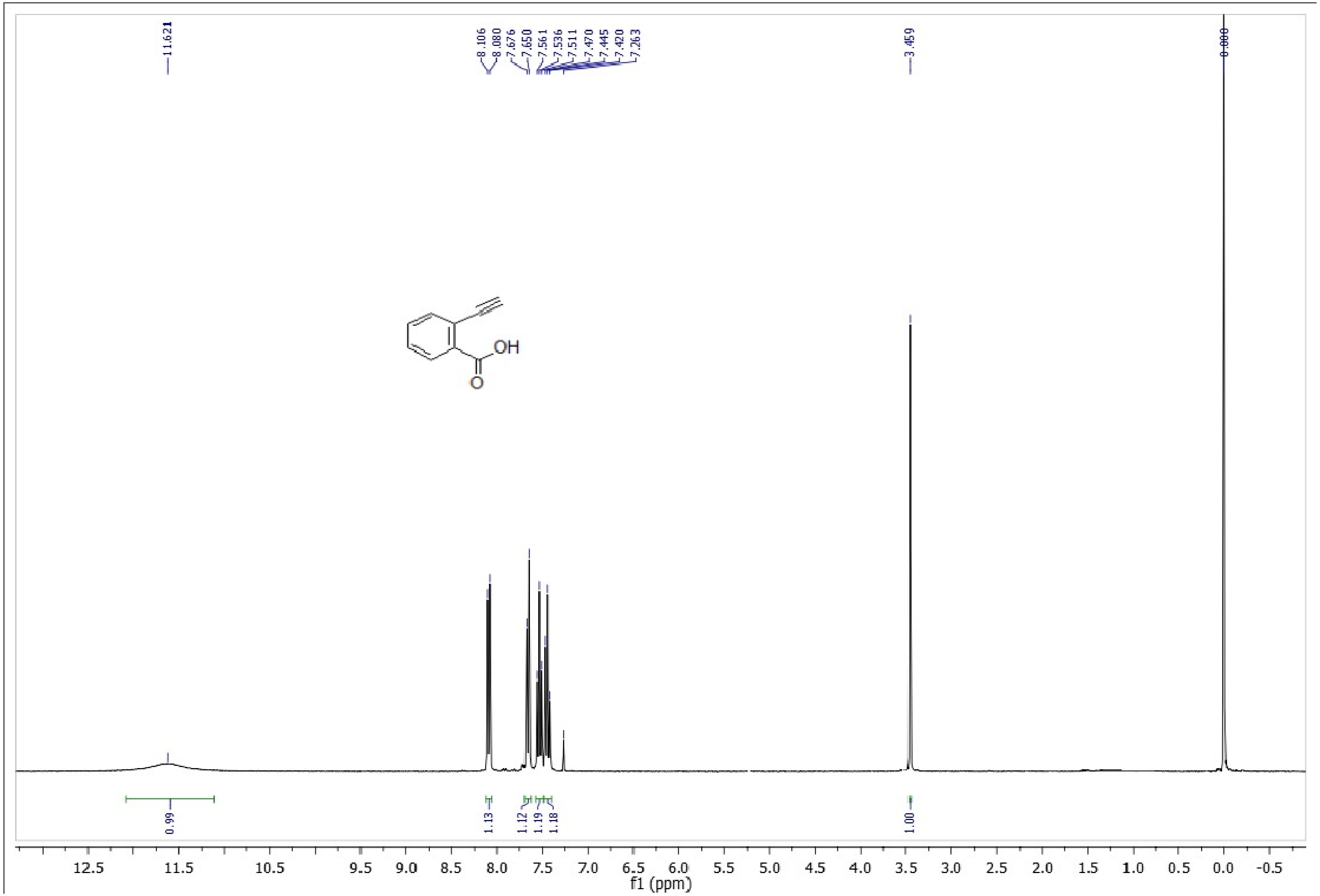


^{13}C NMR(CDCl$_3$)

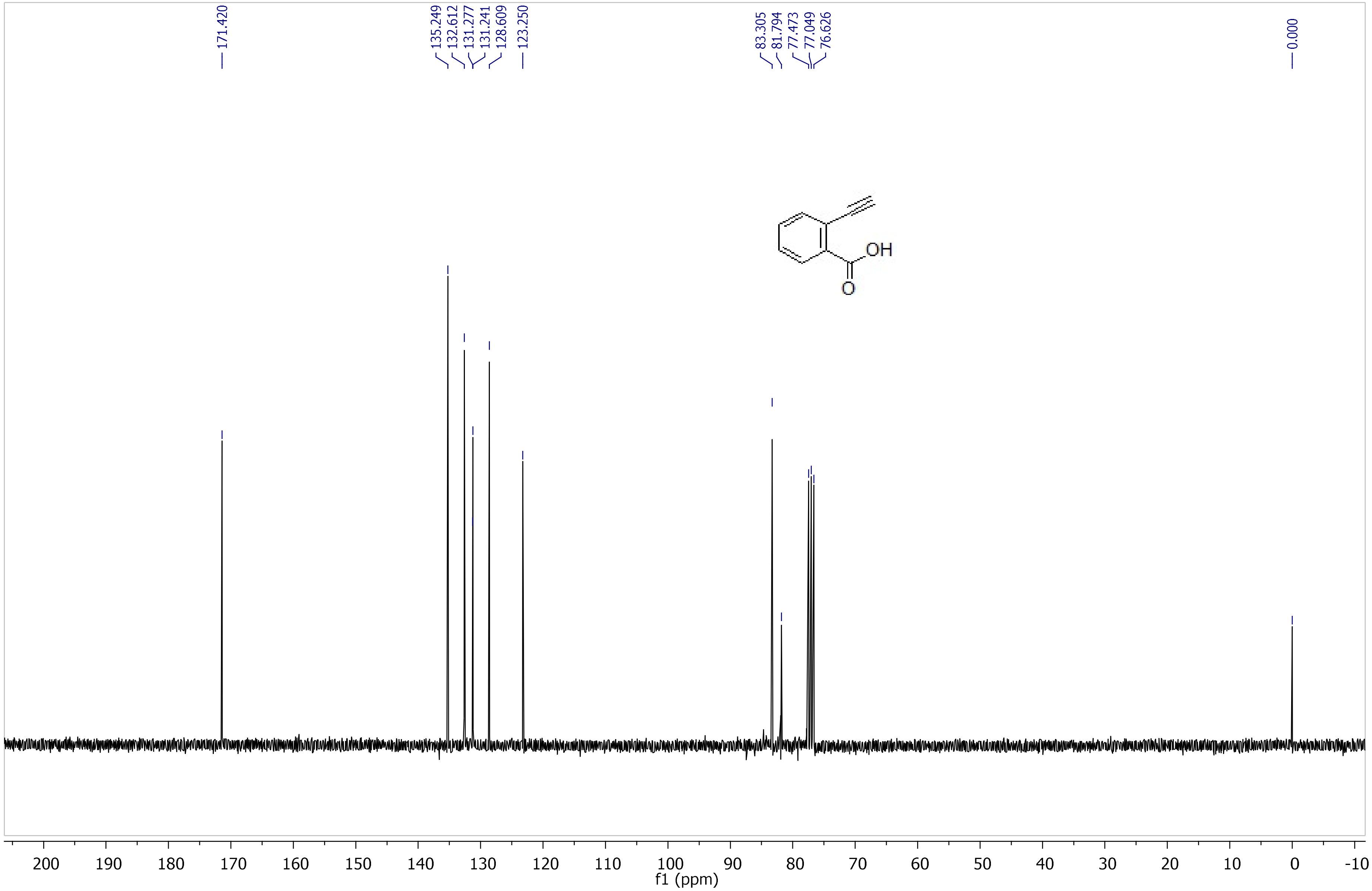


2-Ethynylbenzoic acid (**1j**)

^{1}H NMR(CDCl$_3$)

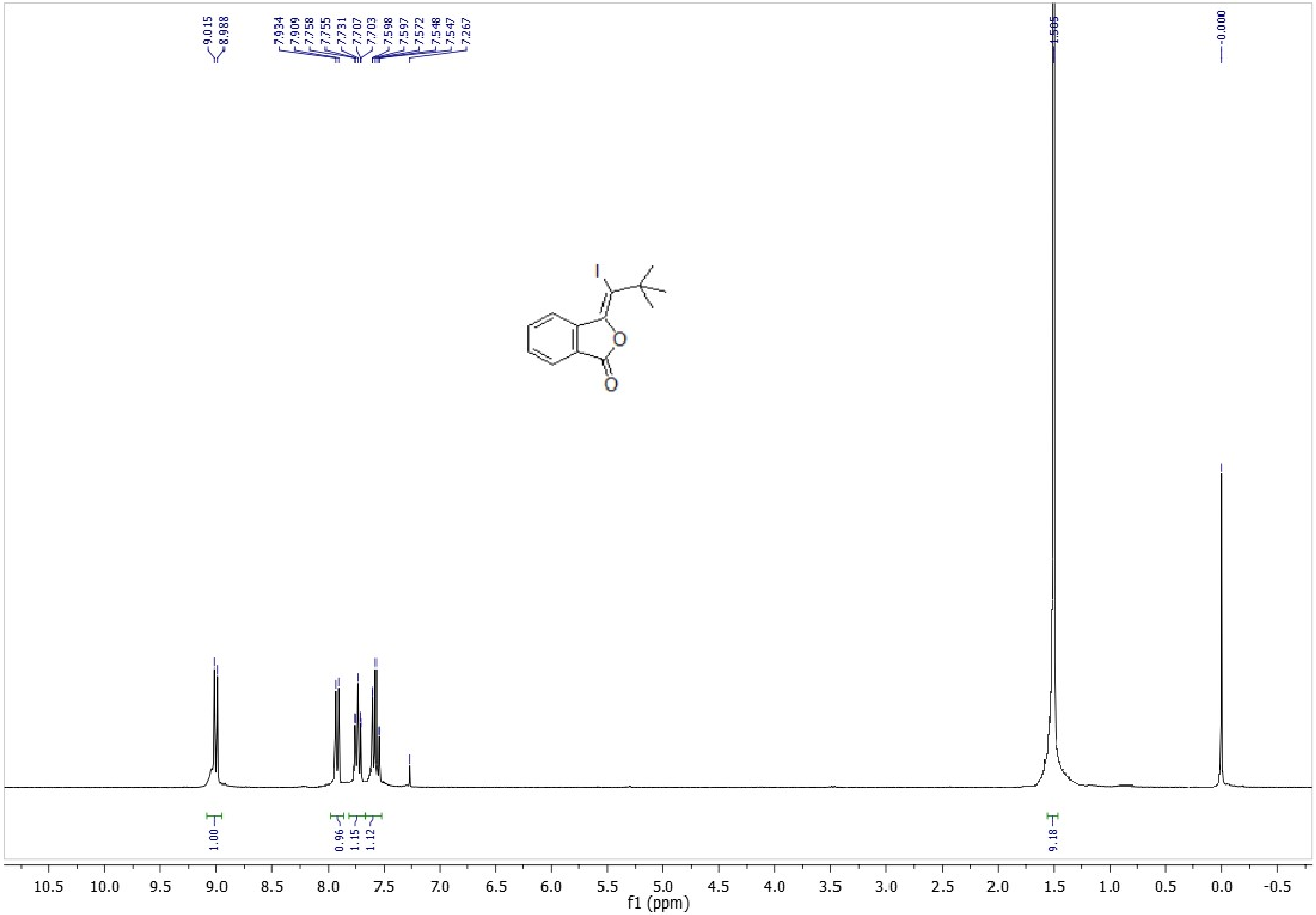


^{13}C NMR($CDCl_3$)

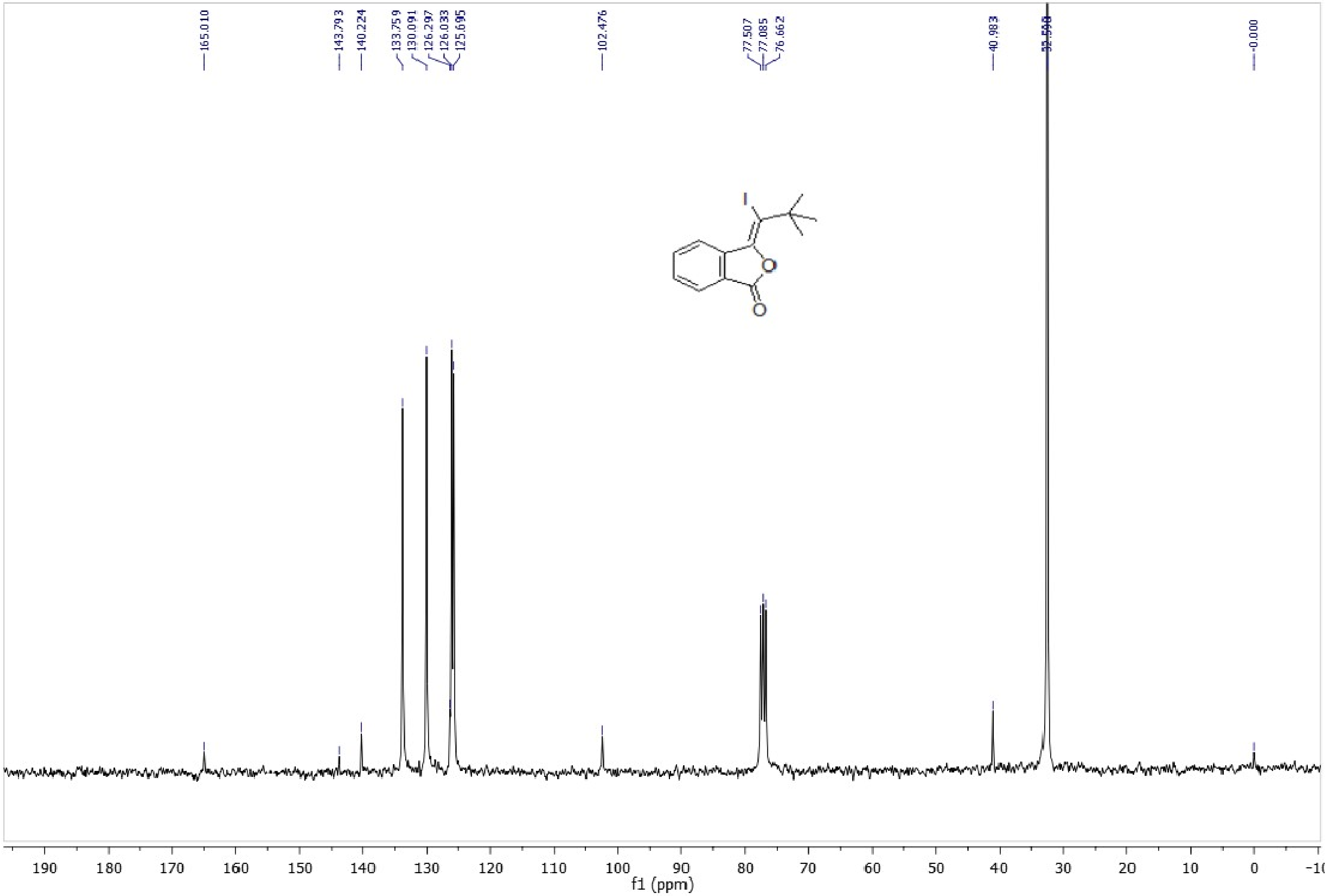


(*E*)-3-(1-Iodo-2,2-dimethylpropylidene)-3H-isobenzofuran-1-one (**2a**)

^{1}H NMR(CDCl$_3$)

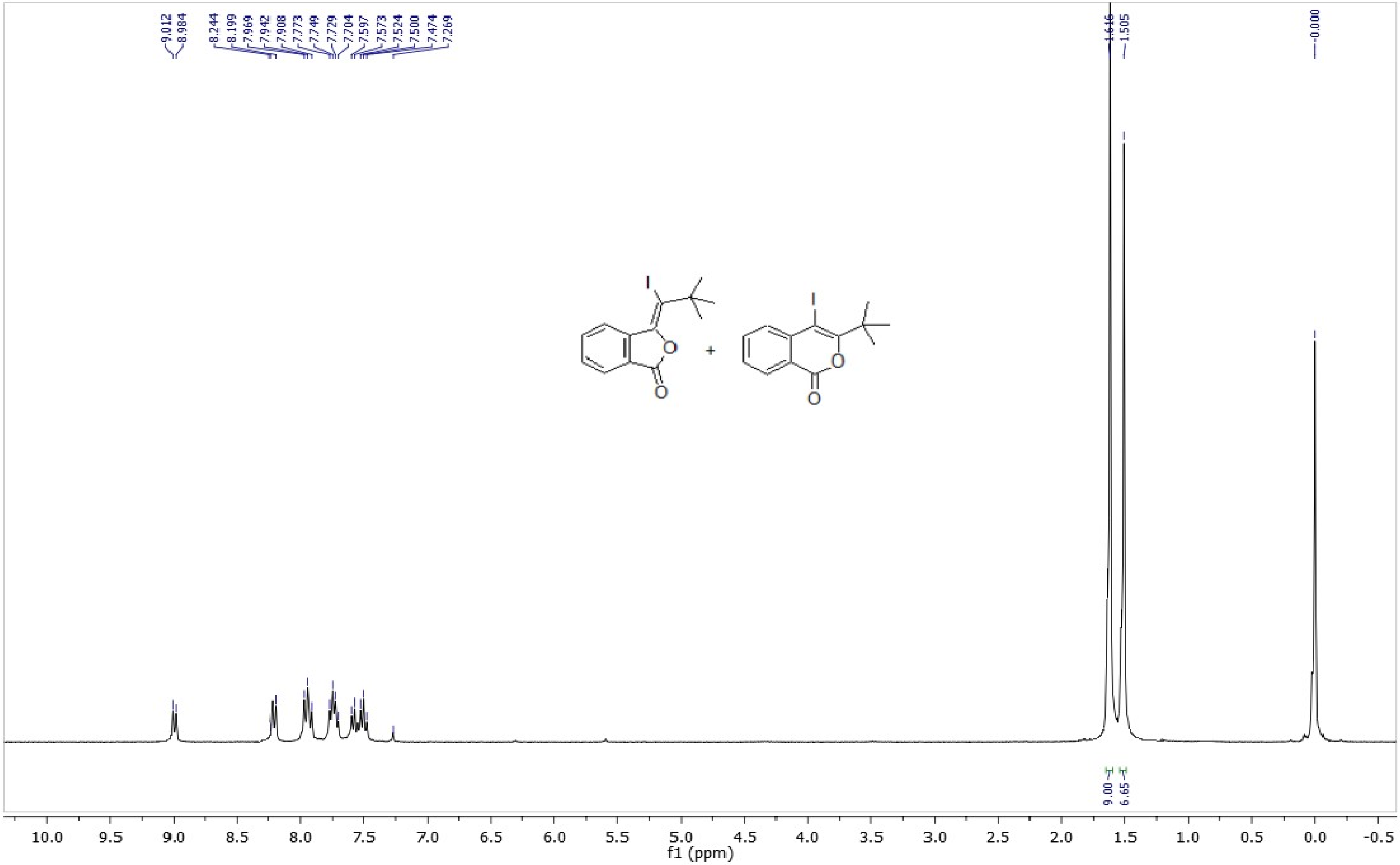


^{13}C NMR(CDCl$_3$)

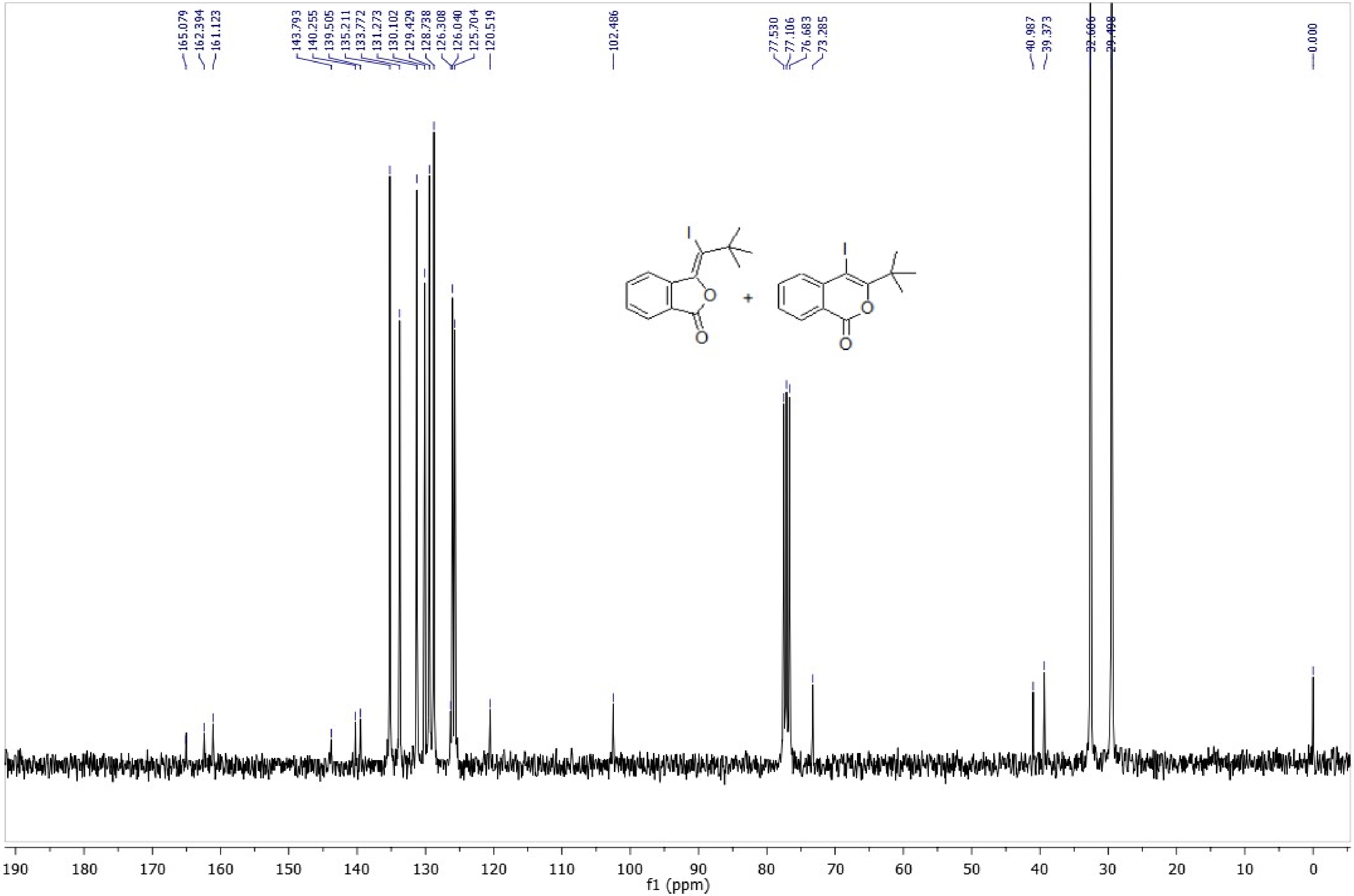


(*E*)-3-(1-Iodo-2,2-dimethylpropylidene)-3H-isobenzofuran-1-one (**2a**) + **3-tert-Butyl-4-iodo-1-isochromen-1-one** (**3a**)

^{1}H NMR(CDCl$_3$)

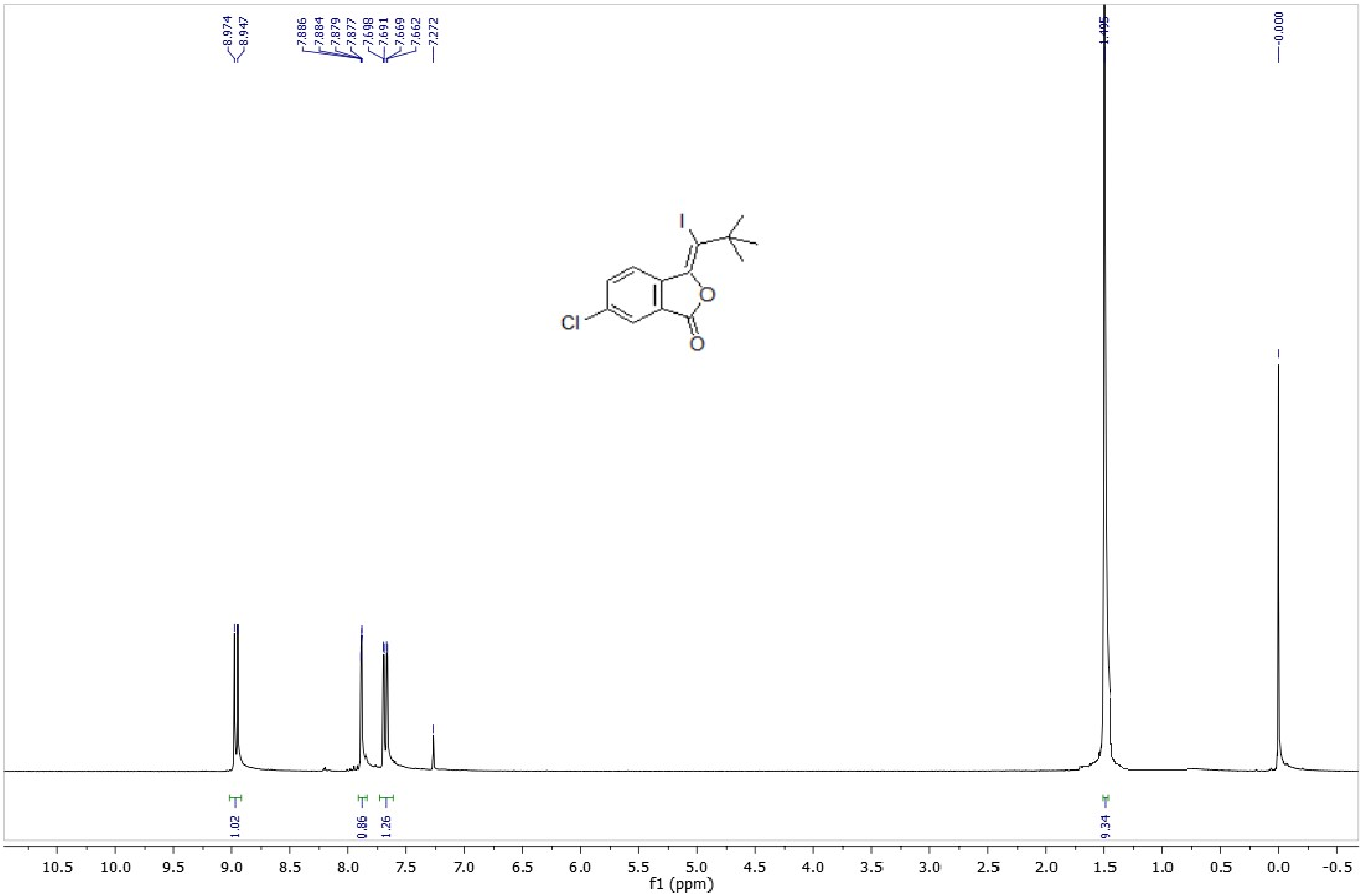


^{13}C NMR(CDCl$_3$)

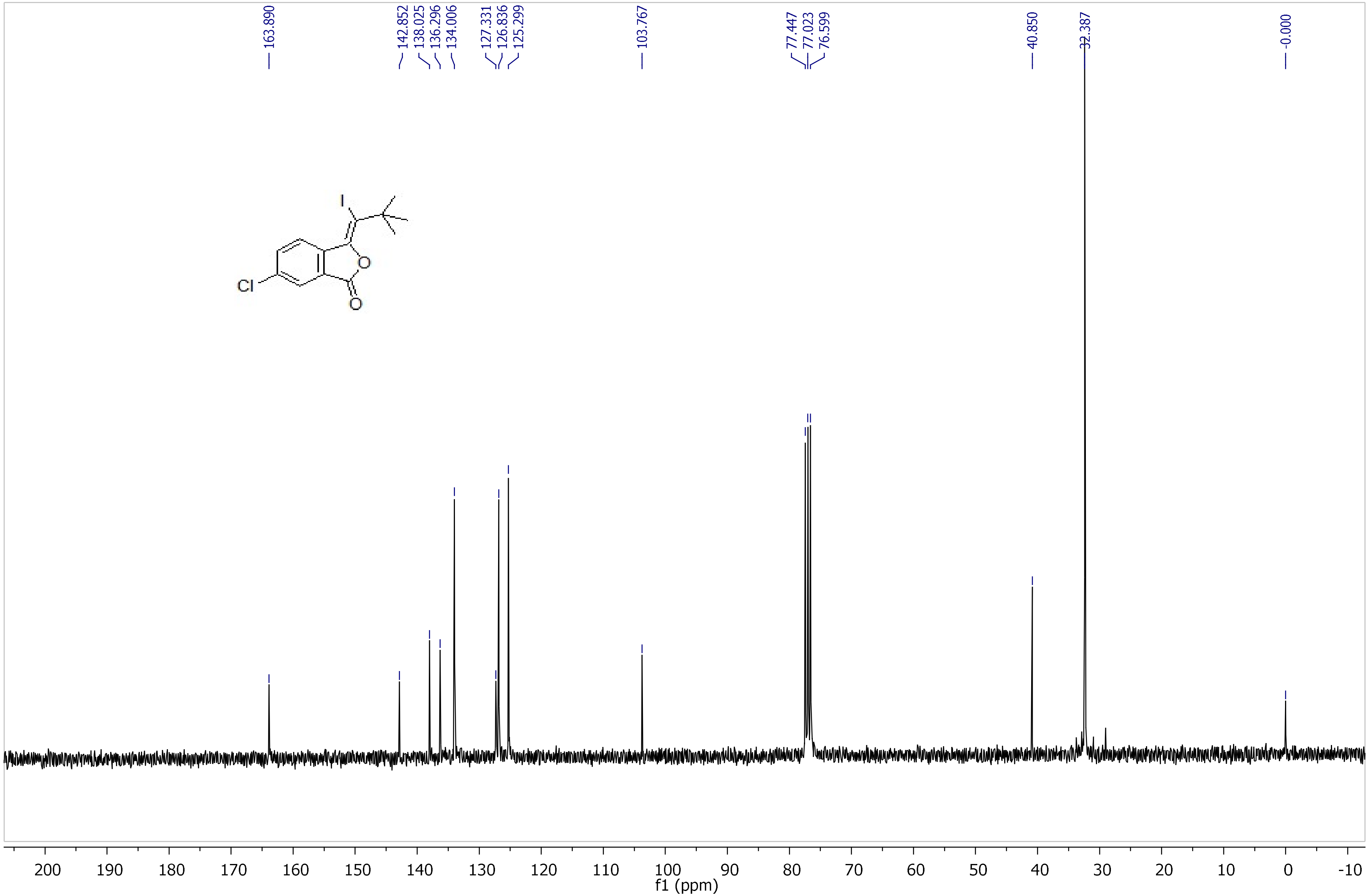


(*E*)-6-Chloro-3-(1-iodo-2,2-dimethylpropylidene)-3H-isobenzofuran-1-one (2b)

^{1}H NMR($CDCl_3$)

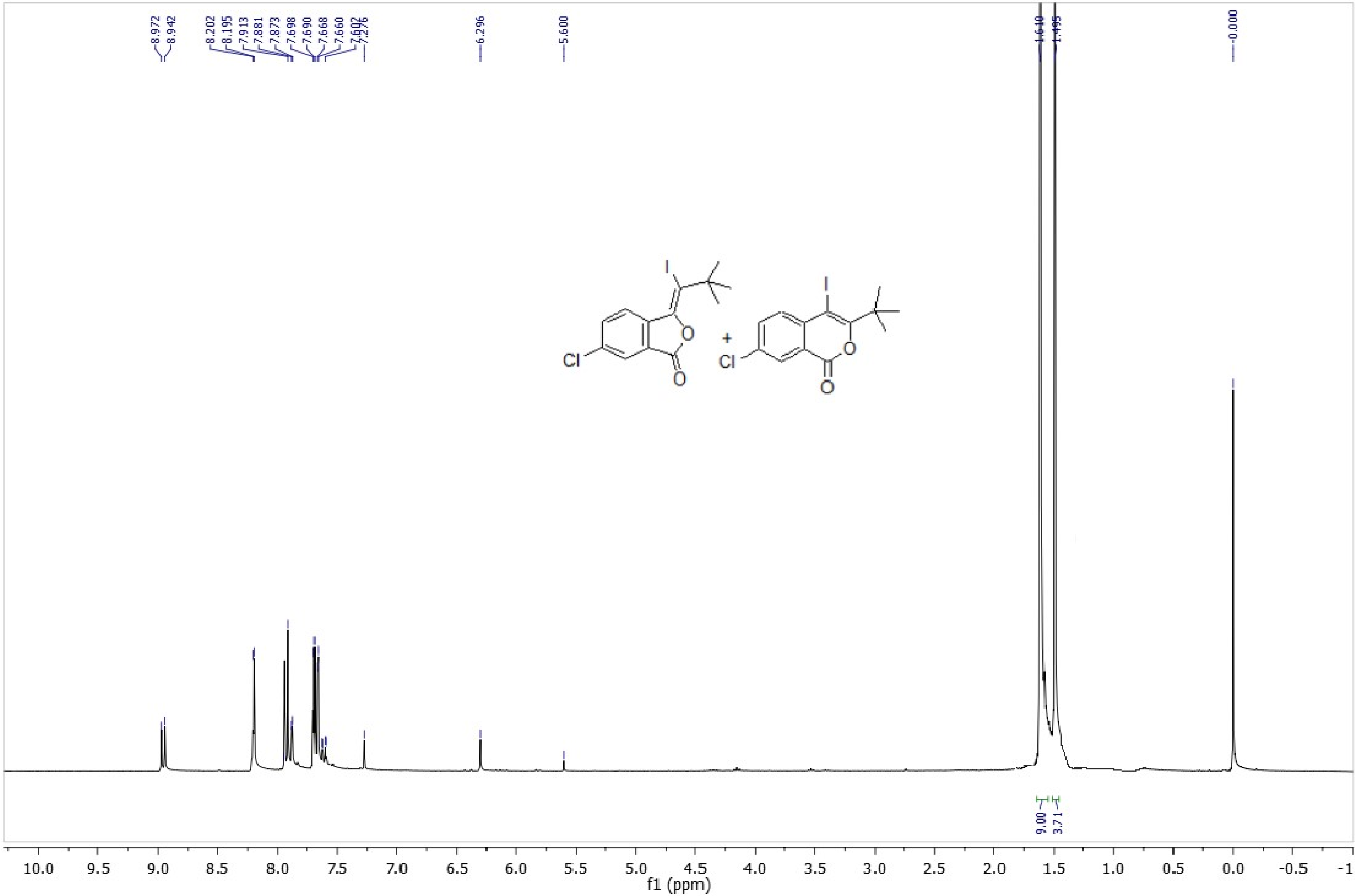


^{13}C NMR(CDCl$_3$)

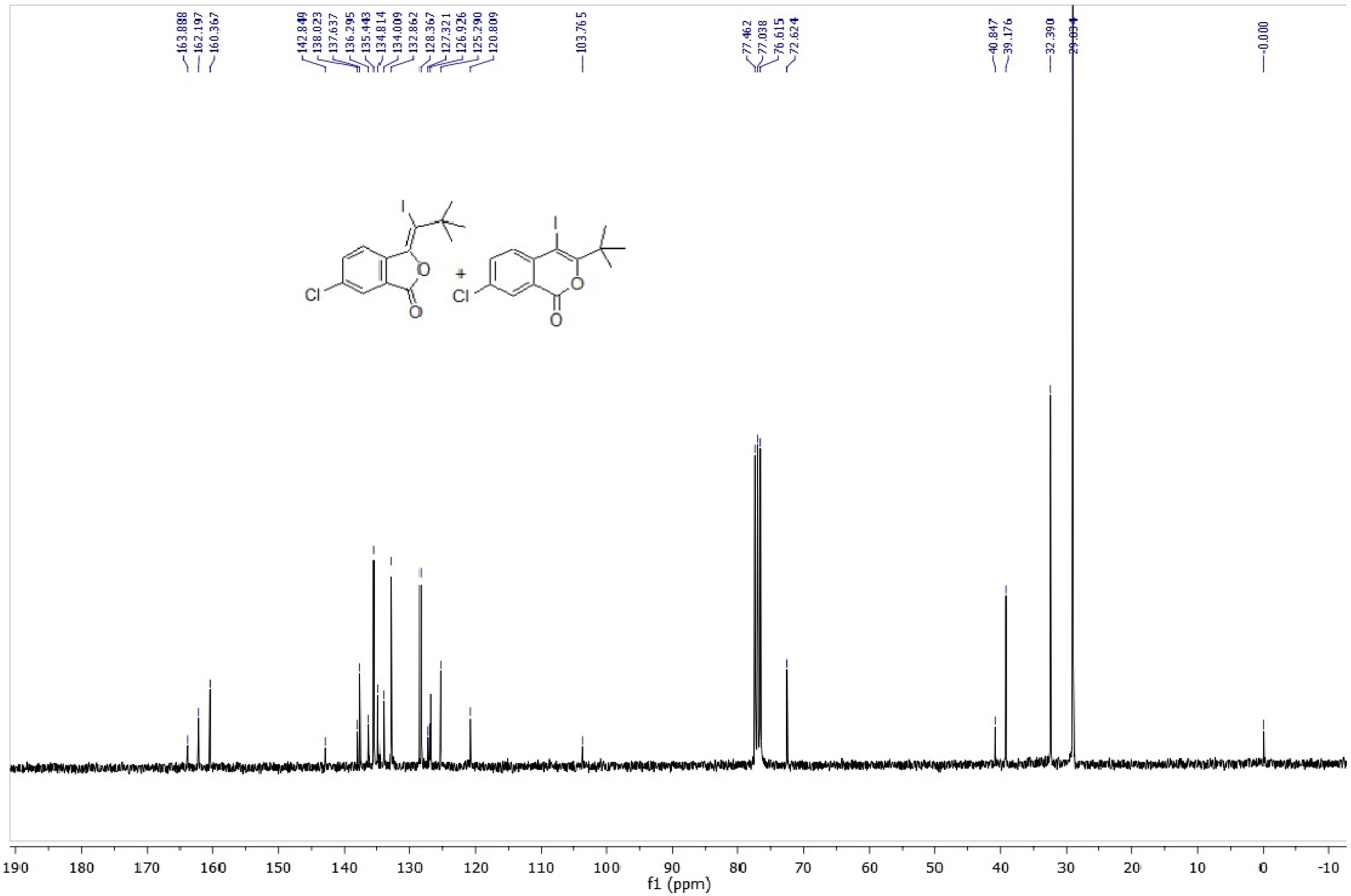


(*E*)-6-Chloro-3-(1-iodo-2,2-dimethylpropylidene)-3H-isobenzofuran-1-one (2b) + **3-tert-Butyl-7-chloro-4-iodo-1-isochromen-1-one (3b)**

^{1}H NMR(CDCl$_3$)

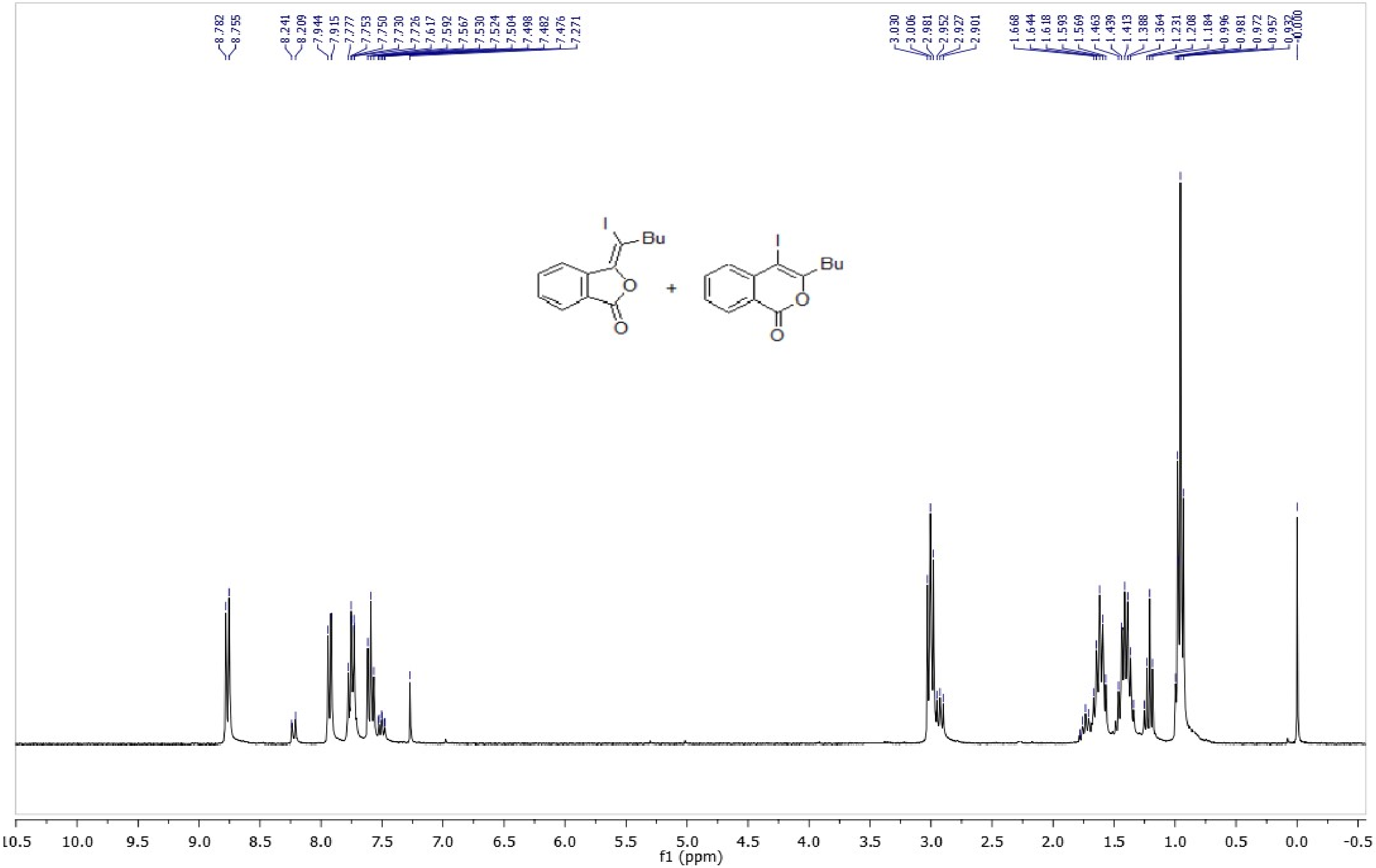


^{13}C NMR(CDCl$_3$)

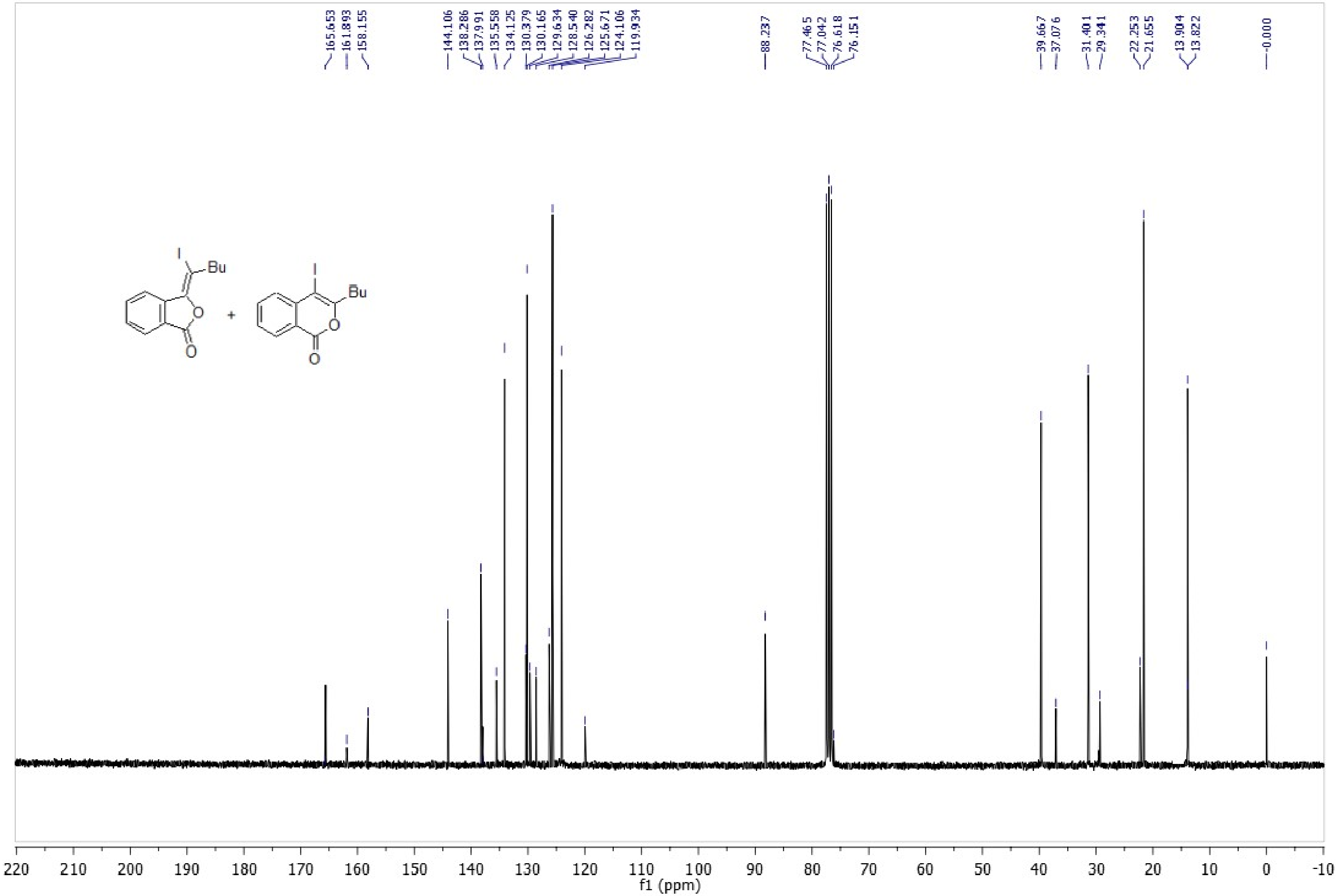


(*E*)-3-(1-Iodopentylidene)-3H-isobenzofuran-1-one (**2c**) + **3-Butyl-4-iodo-1-isochromen-1-one** (**3c**)

^{1}H NMR(CDCl$_3$)

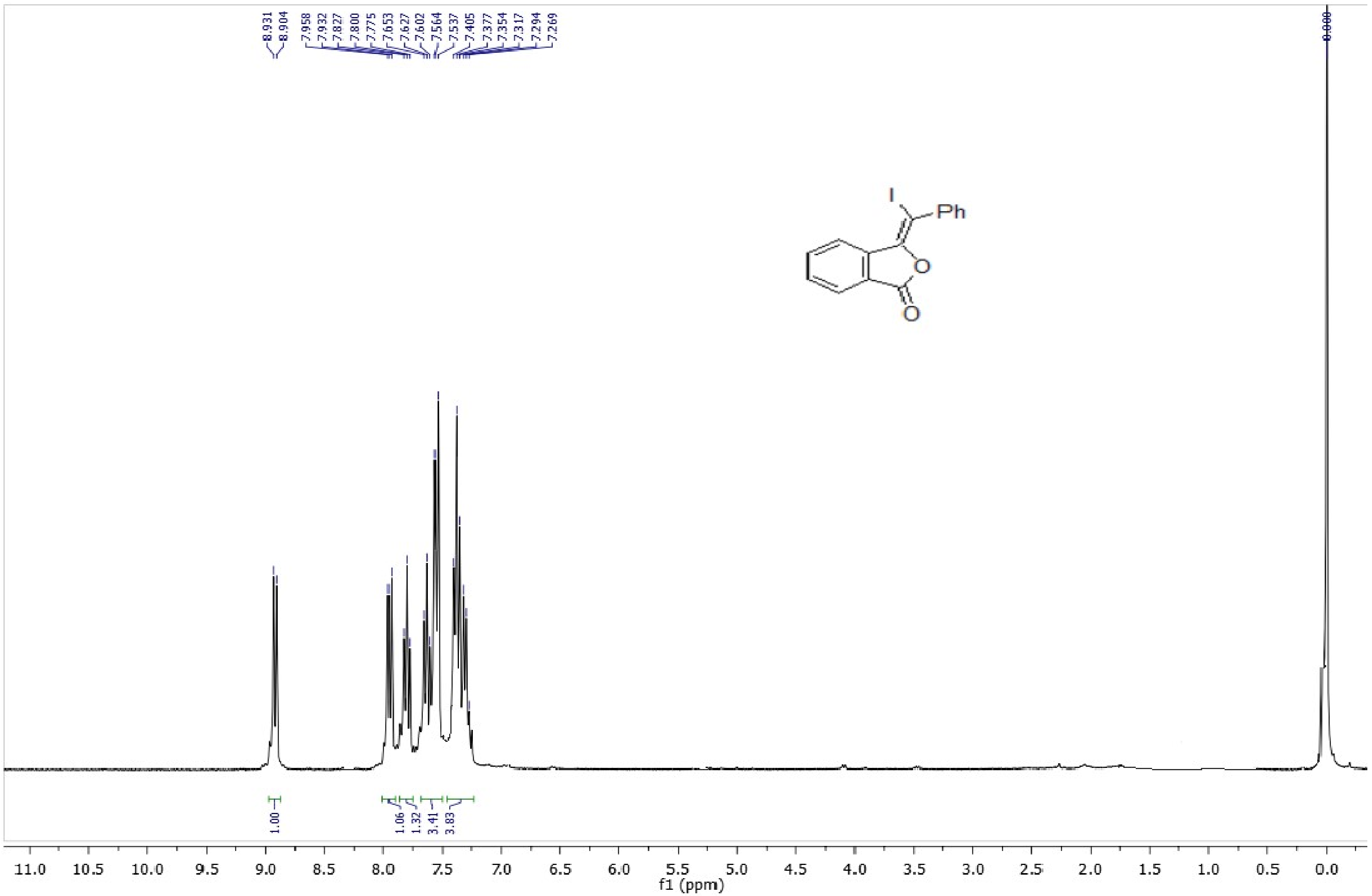


^{13}C NMR(CDCl$_3$)

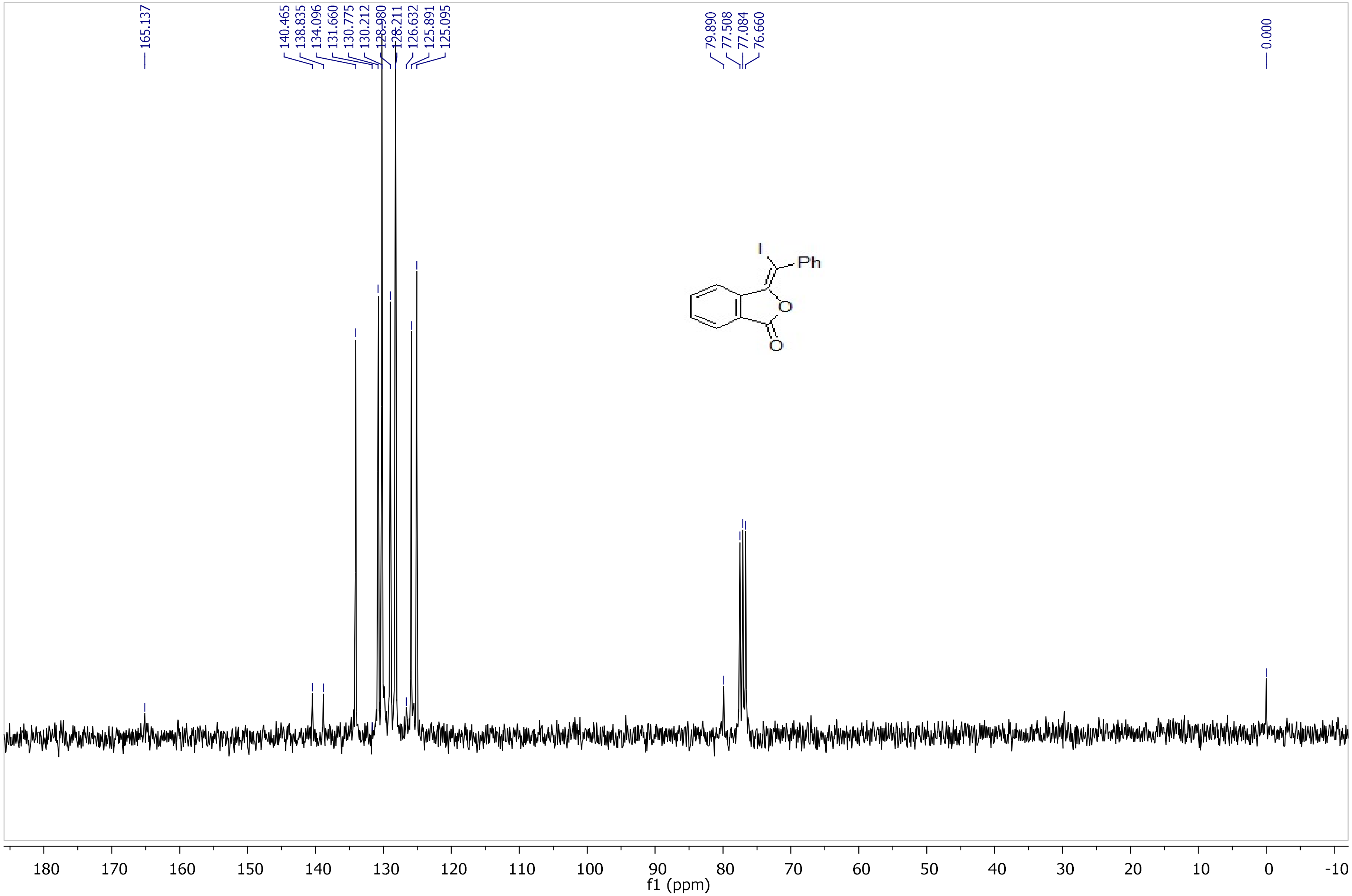


(*E*)-3-(Iodophenylmethylene)-3H-isobenzofuran-1-one (2d)

^{1}H NMR($CDCl_3$)

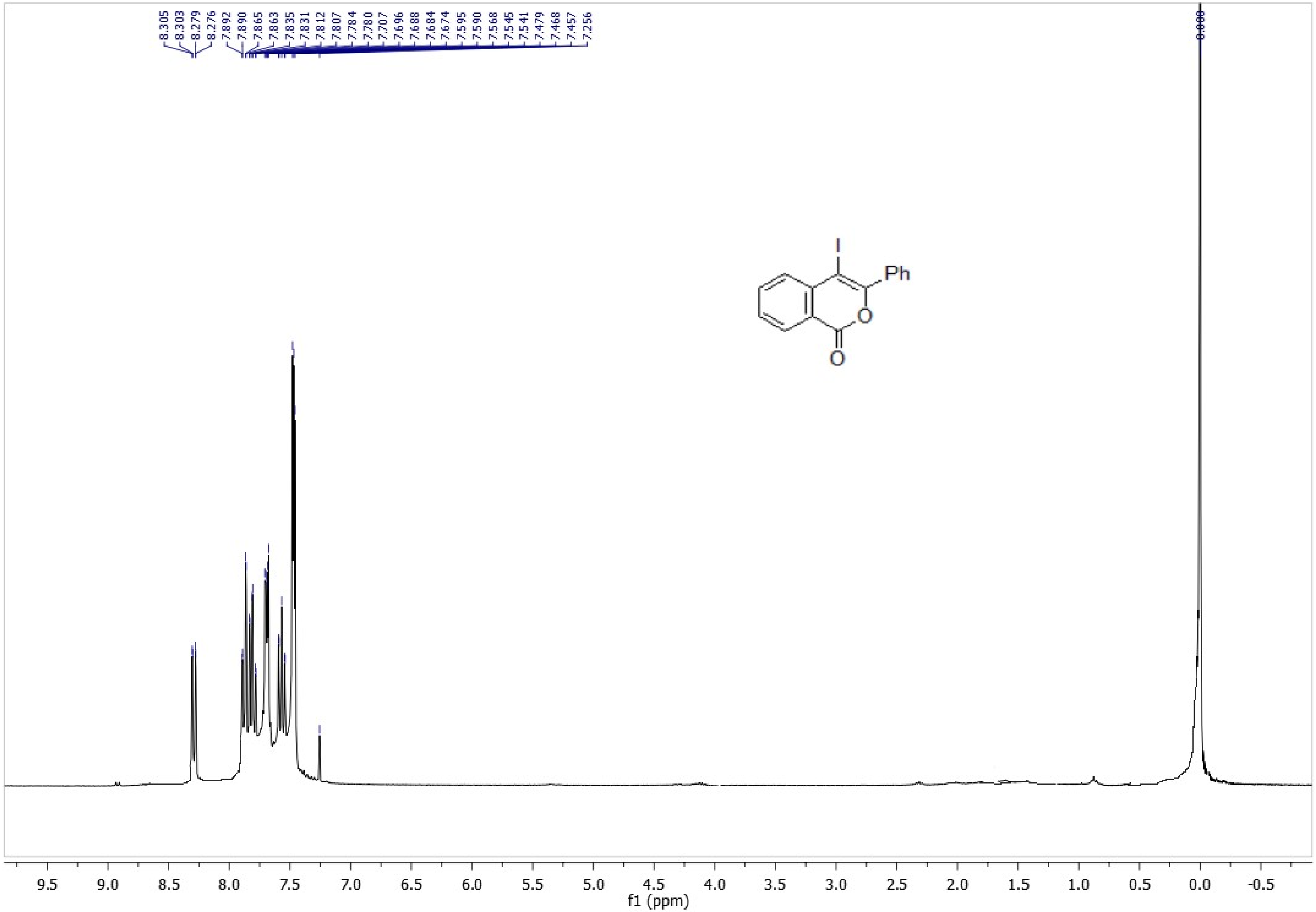


^{13}C NMR(CDCl$_3$)

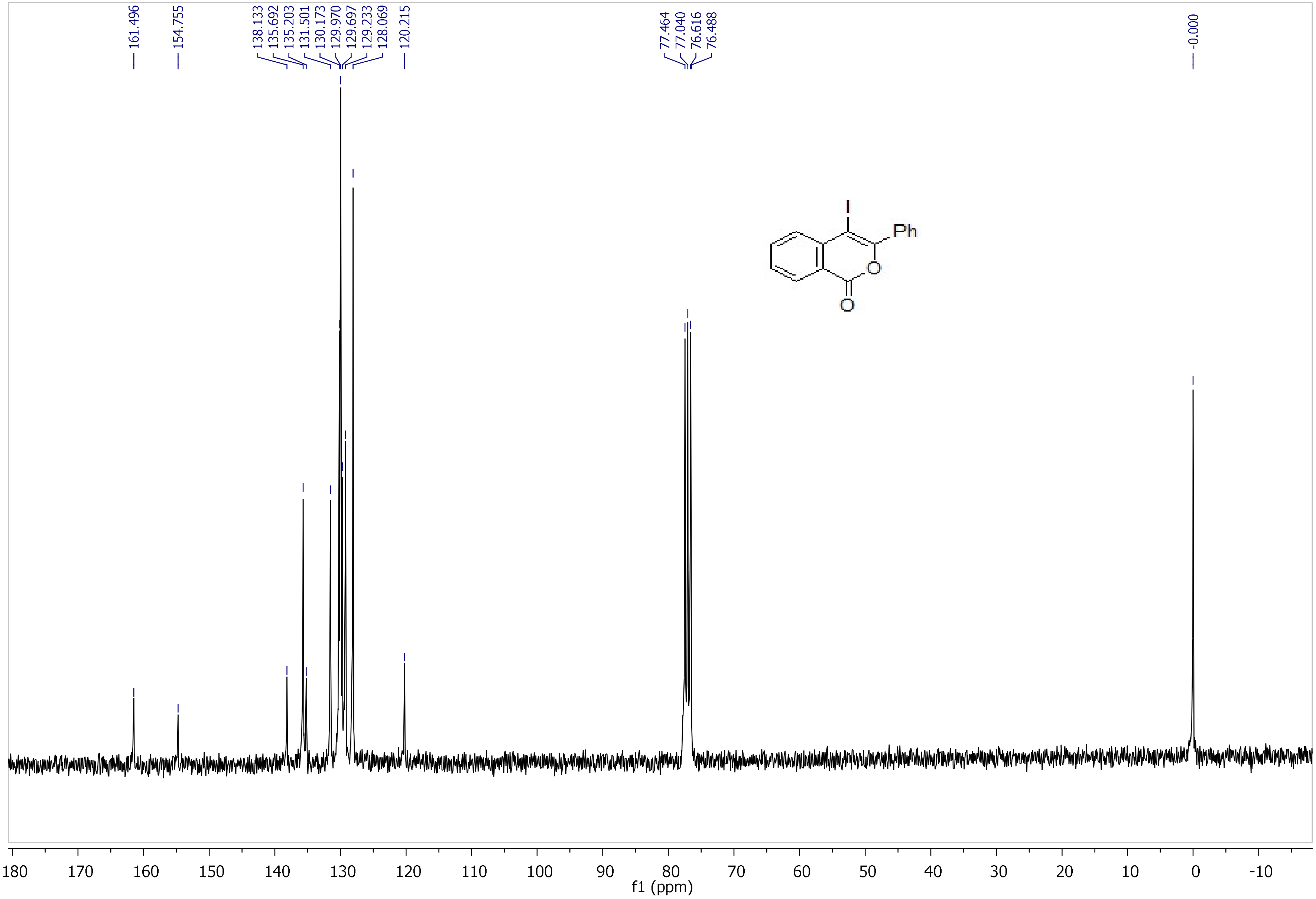


4-Iodo-3-phenylisochromen-1-one (**3d**)

^{1}H NMR(CDCl$_3$)

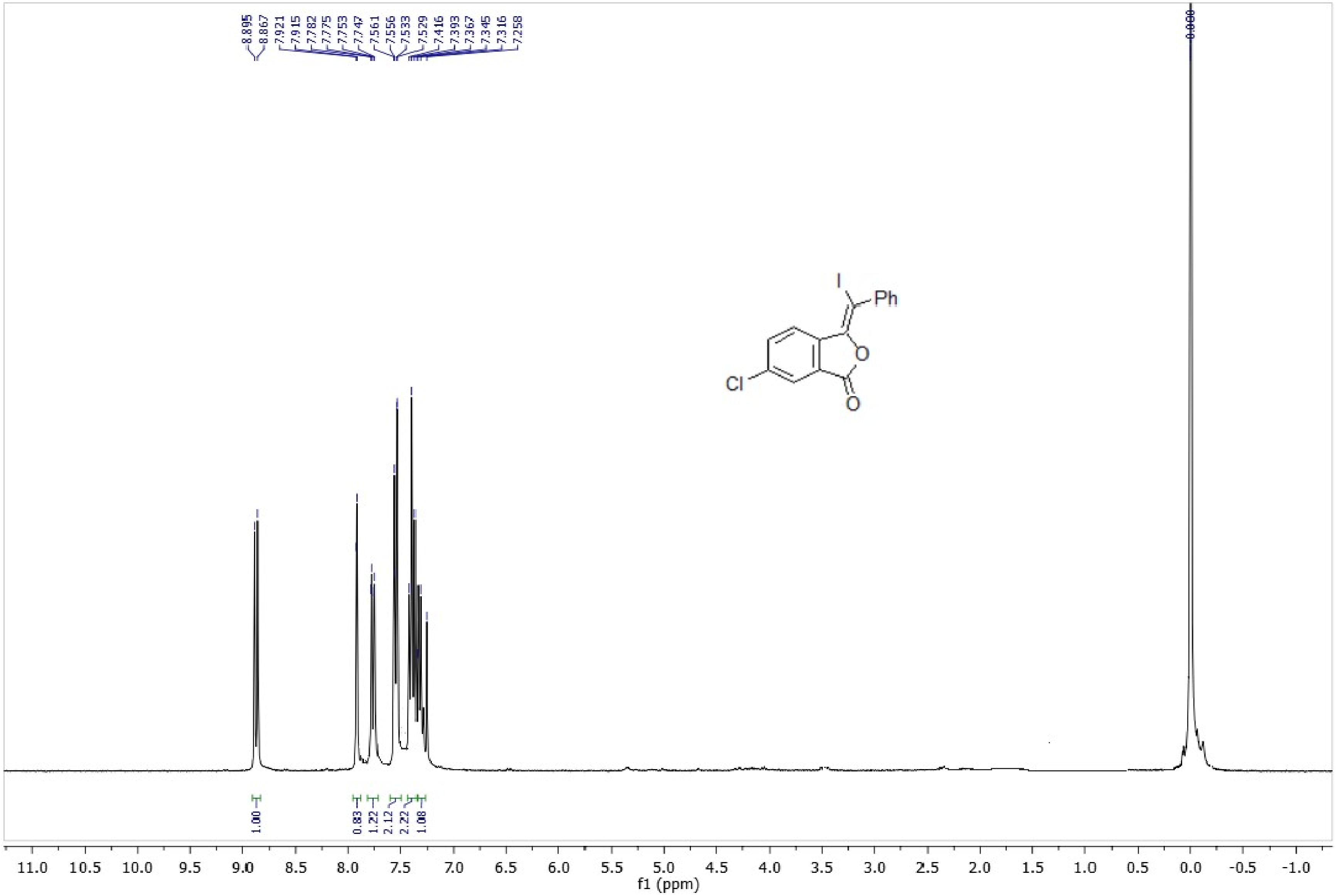


^{13}C NMR(CDCl$_3$)

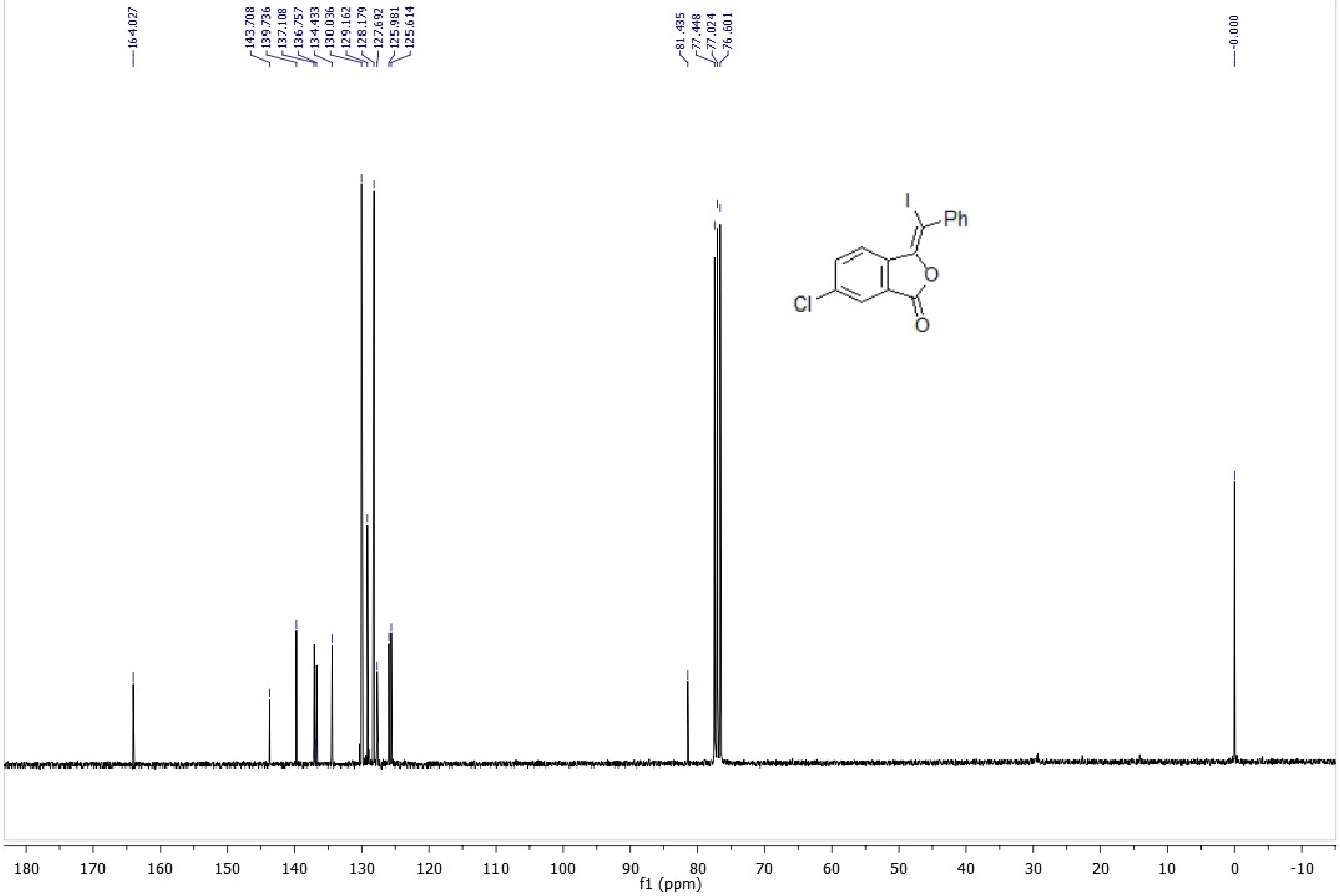


(*E*)-6-Chloro-3-(iodophenylmethylene)-3H-isobenzofuran-1-one (**2e**)

^{1}H NMR(CDCl$_3$)

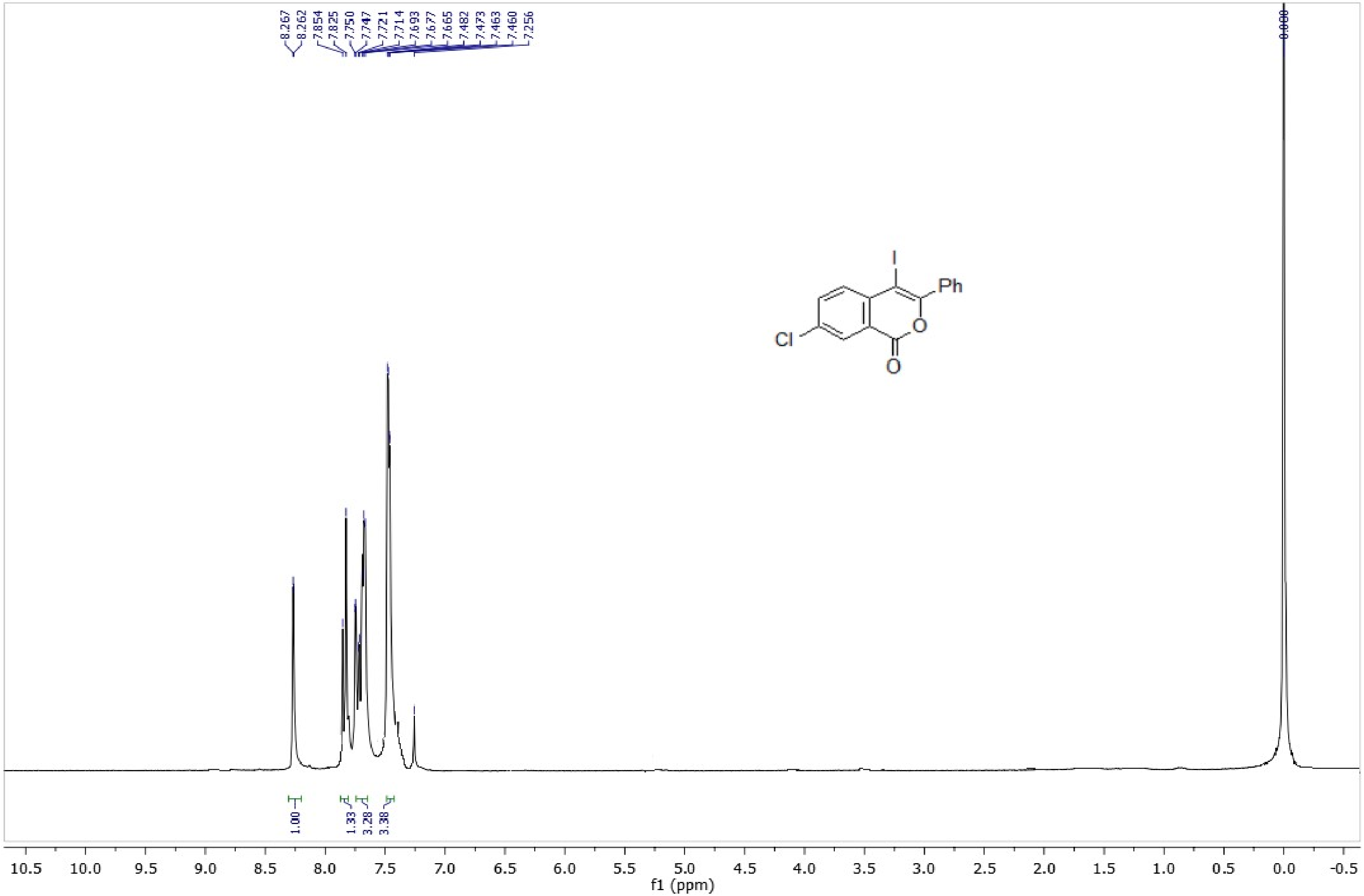


^{13}C NMR(CDCl$_3$)

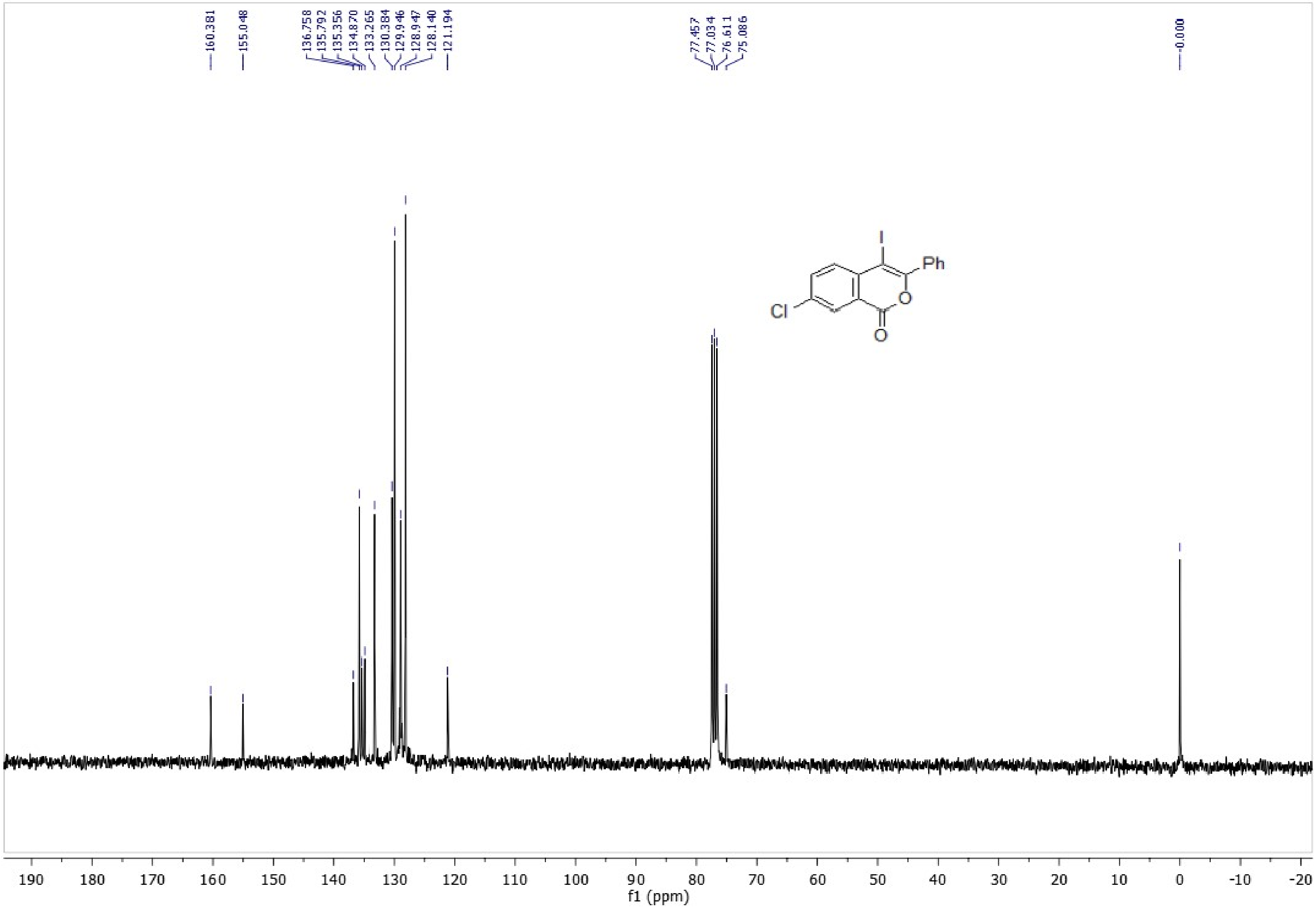


7-Chloro-4-iodo-3-phenylisochromen-1-one (**3e**)

^{1}H NMR(CDCl$_3$)

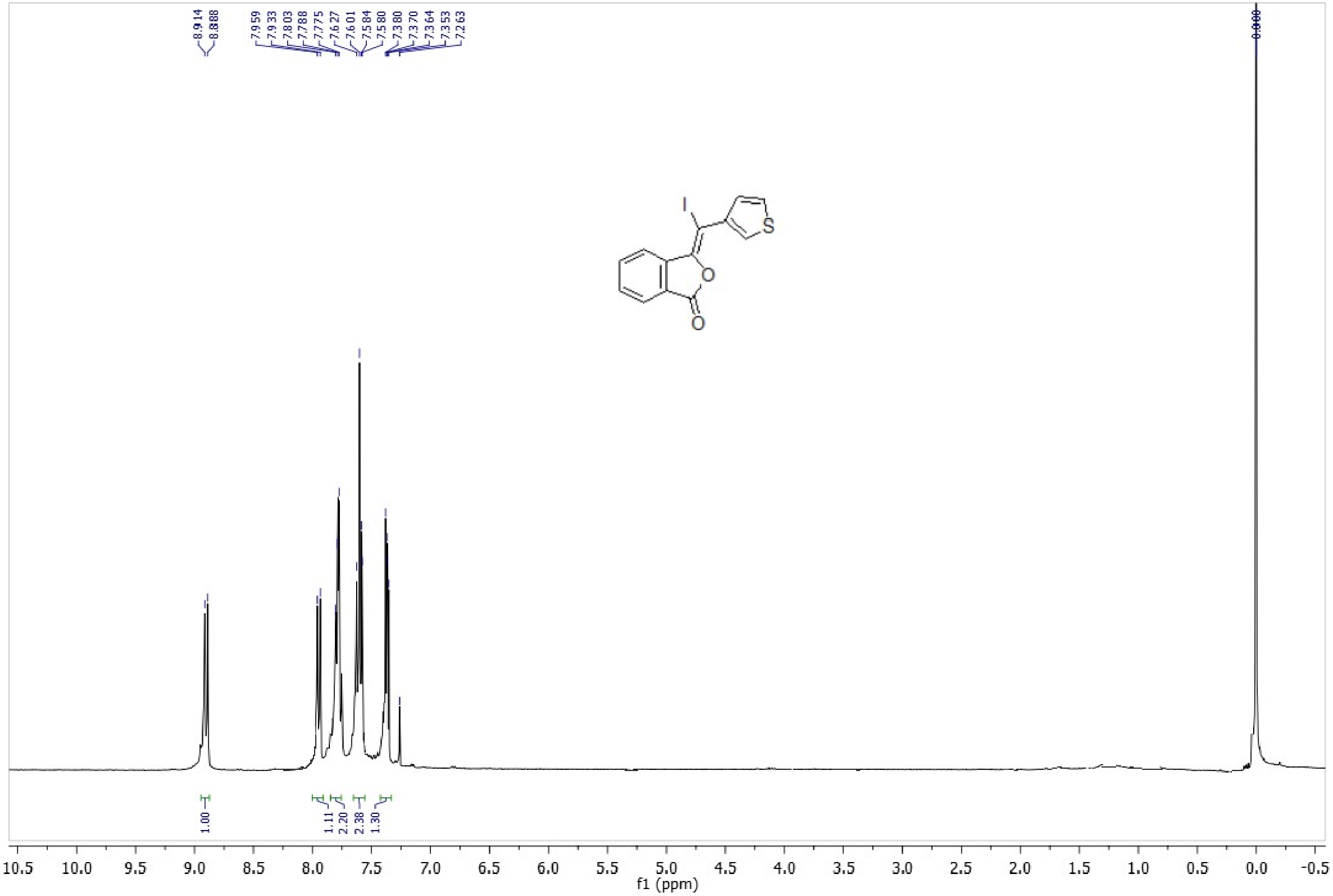


^{13}C NMR(CDCl$_3$)

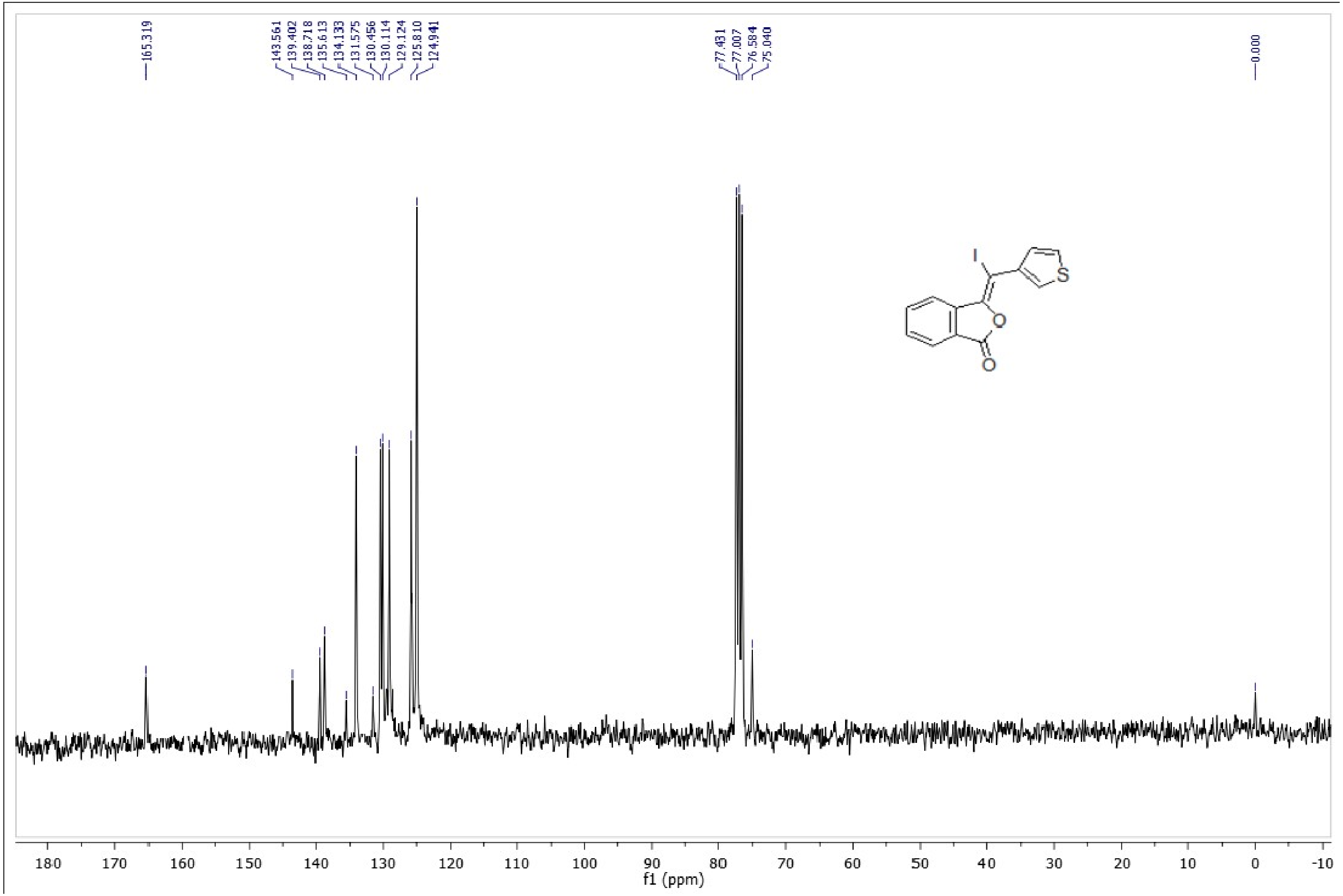


(*E*)-3-(Iodothiophen-3-yl-methylene)-3H-isobenzofuran-1-one (2f)

^{1}H NMR(CDCl$_3$)

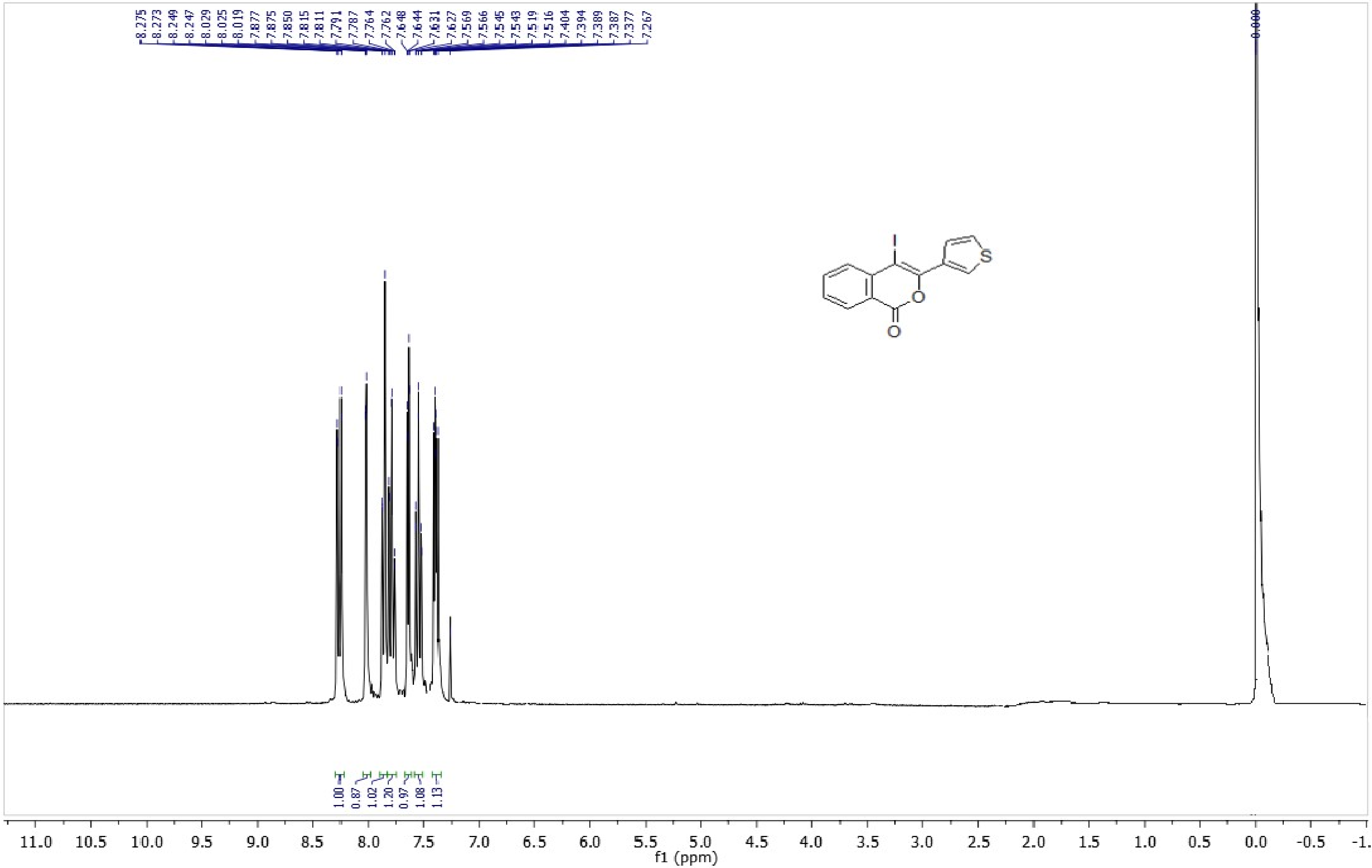


^{13}C NMR(CDCl$_3$)

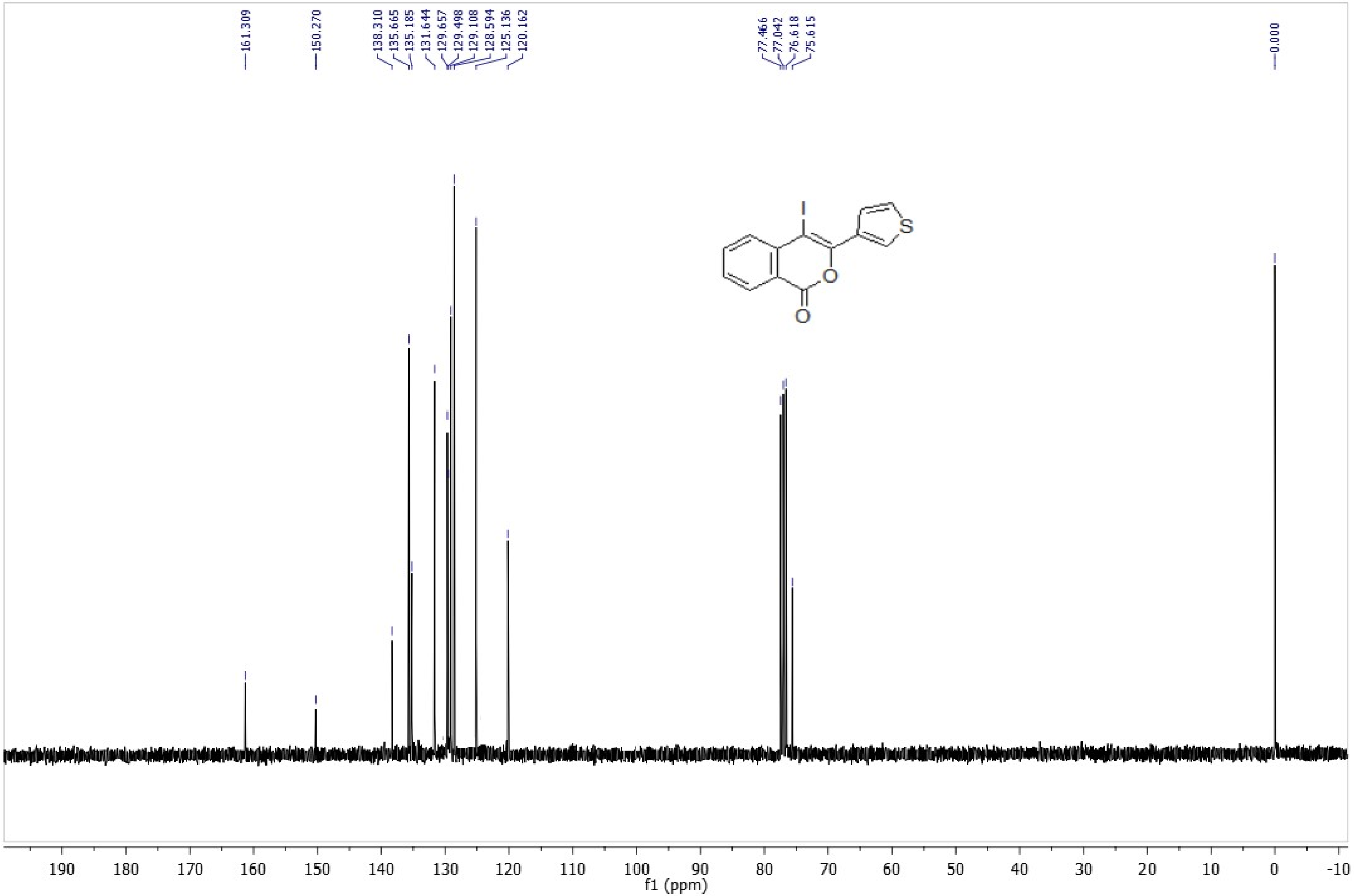


4-Iodo-3-thiophen-3-ylisochromen-1-one (**3f**)

^{1}H NMR(CDCl$_3$)

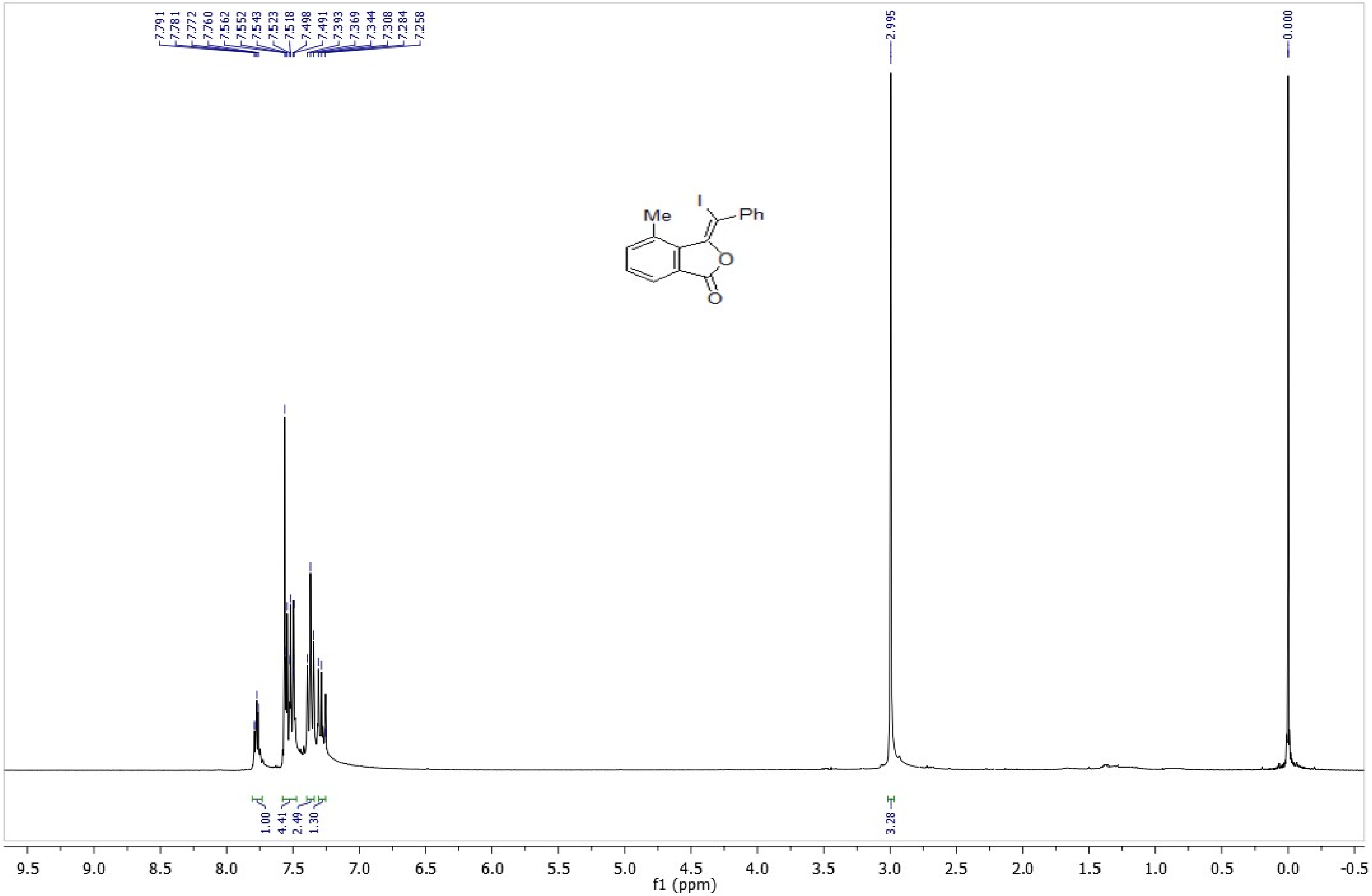


^{13}C NMR(CDCl$_3$)

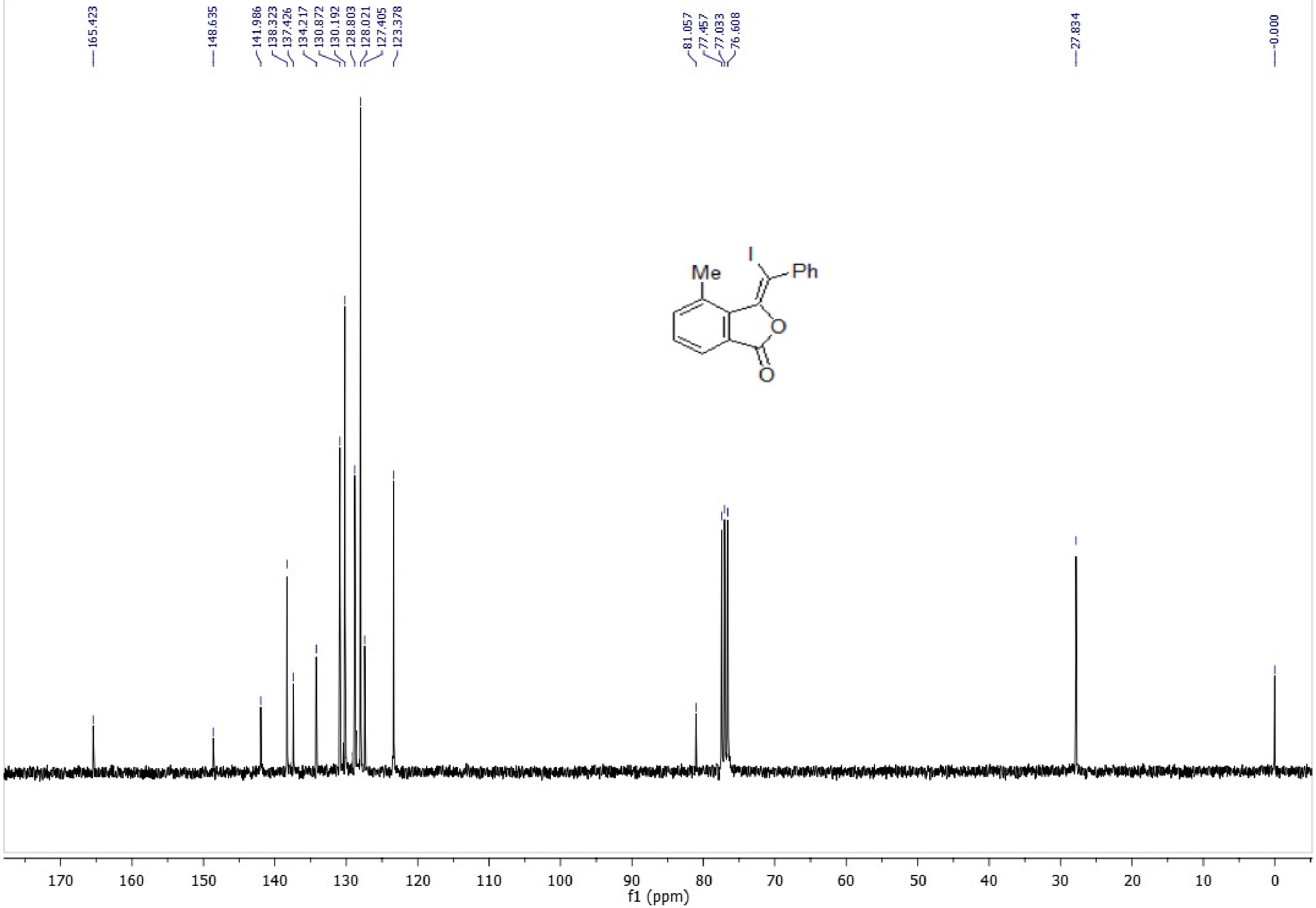


(*E*)-3-(Iodophenylmethylene)-4-methyl-3H-isobenzofuran-1-one (2g)

^{1}H NMR(CDCl$_3$)

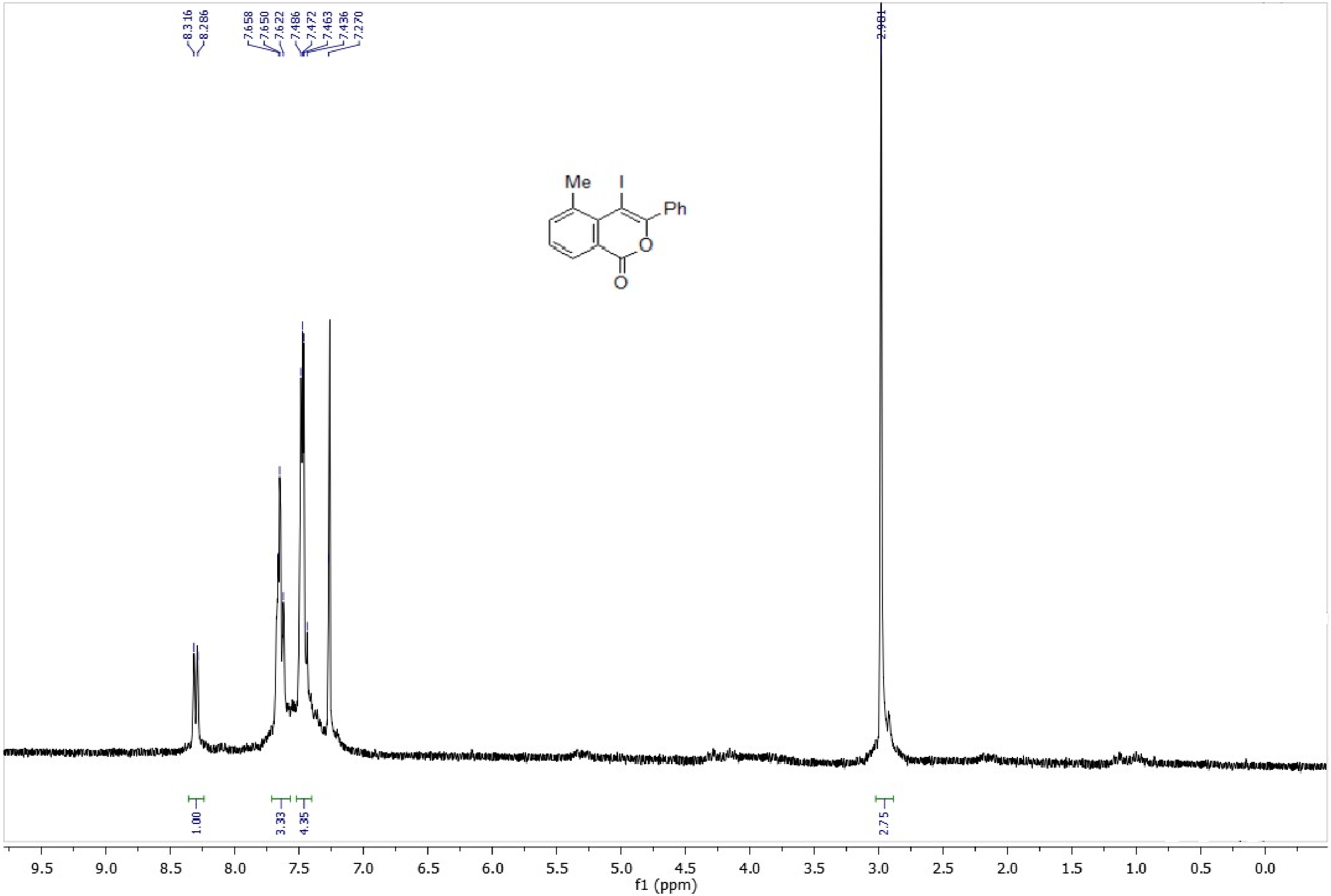


^{13}C NMR(CDCl$_3$)

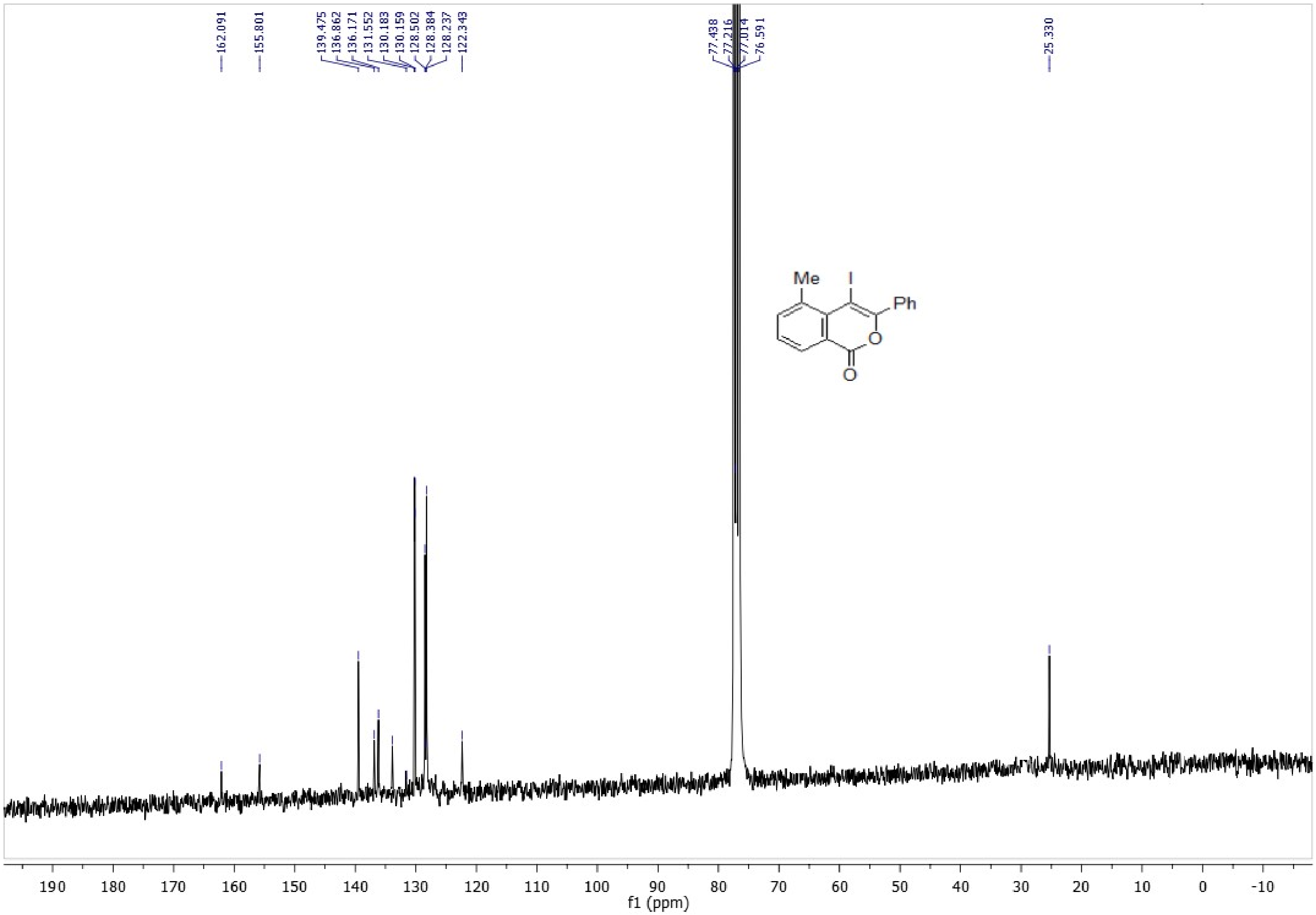


4-Iodo-5-methyl-3-phenylisochromen-1-one (**3g**)

^{1}H NMR(CDCl$_3$)

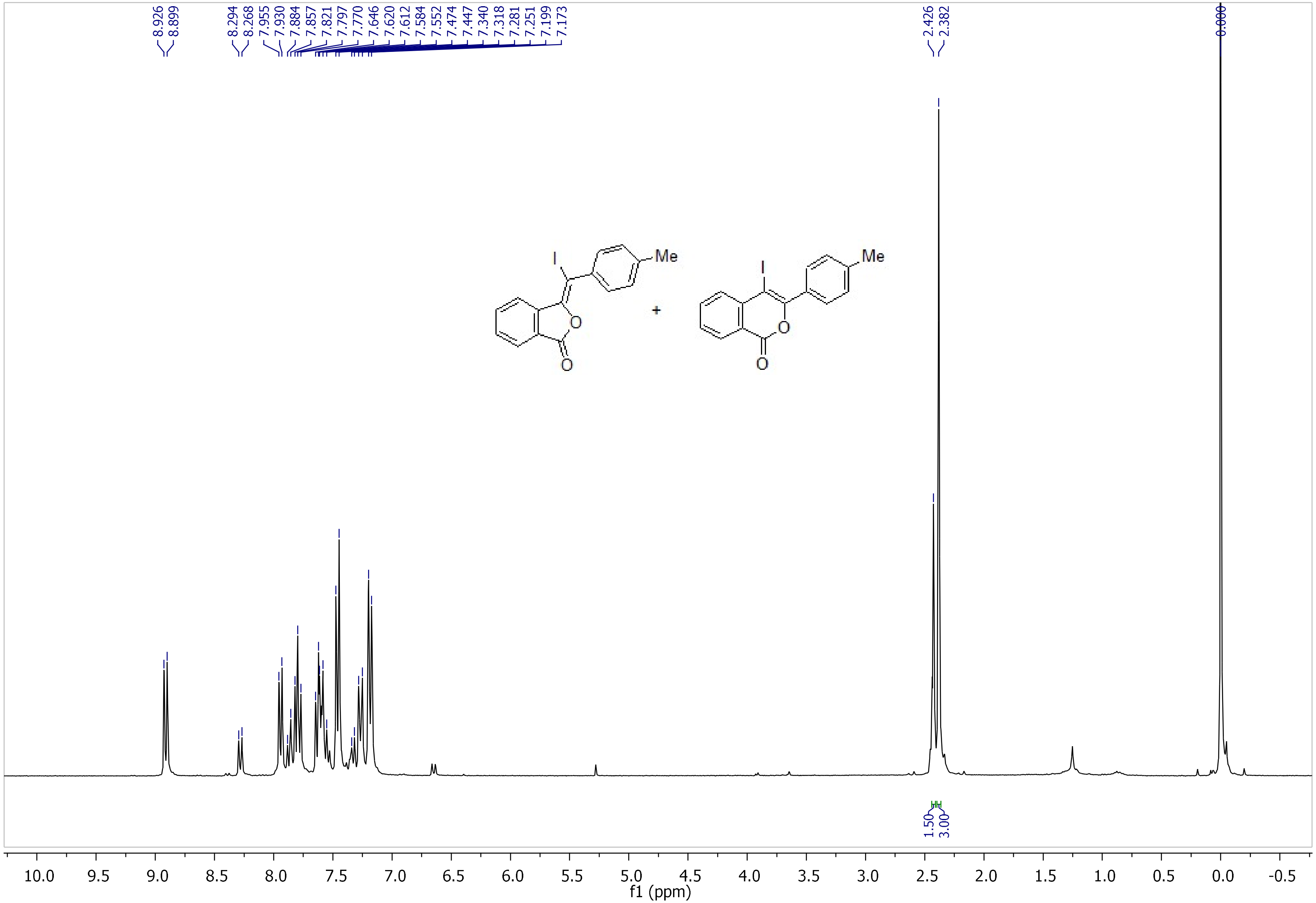


^{13}C NMR(CDCl$_3$)

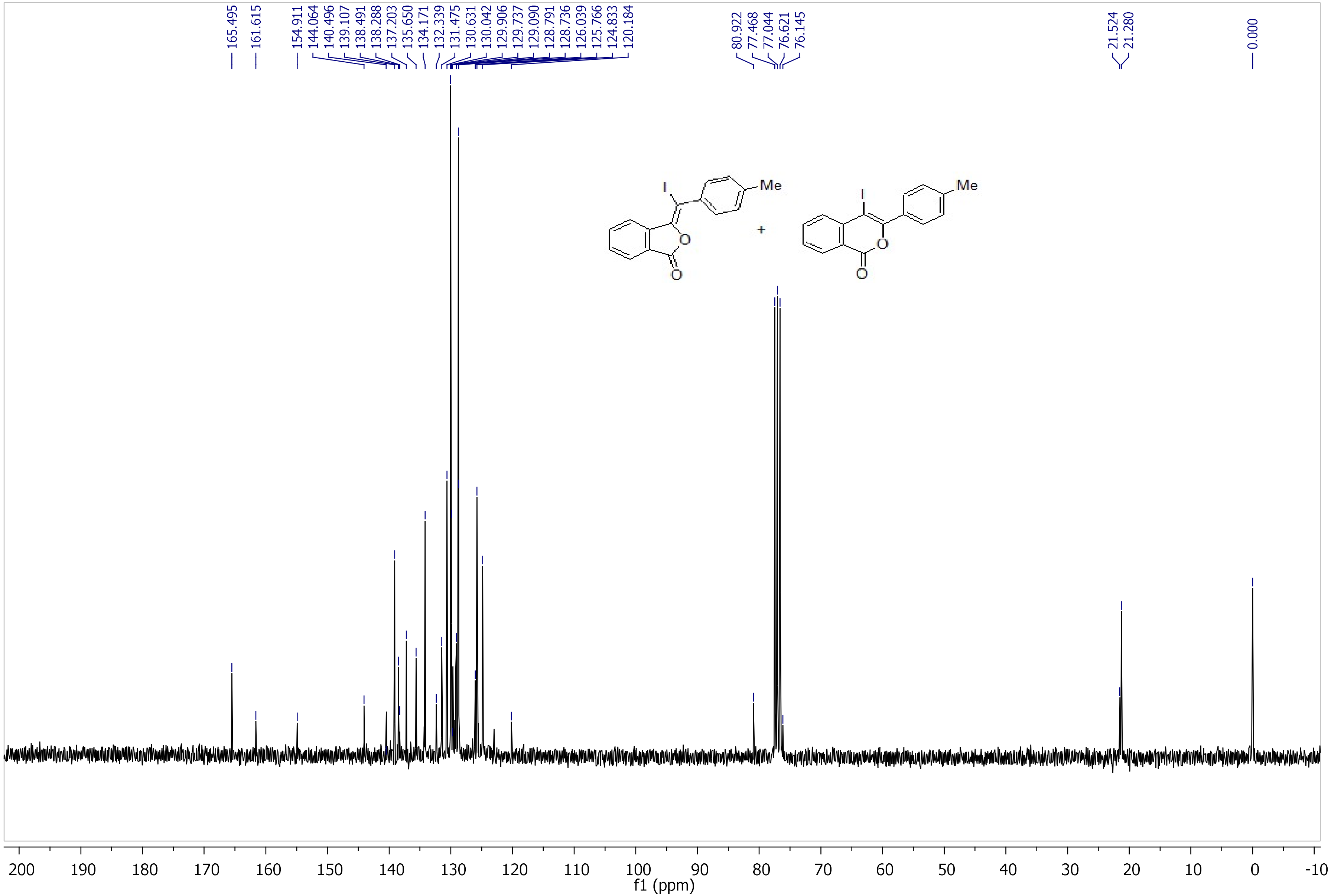


3-(Iodo-p-tolylmethylene)-3H-isobenzofuran-1-one (**2h**) + **4-(Iodo-3-p-tolylisochromen-1-one** (**3h**)

^{1}H NMR(CDCl$_3$)

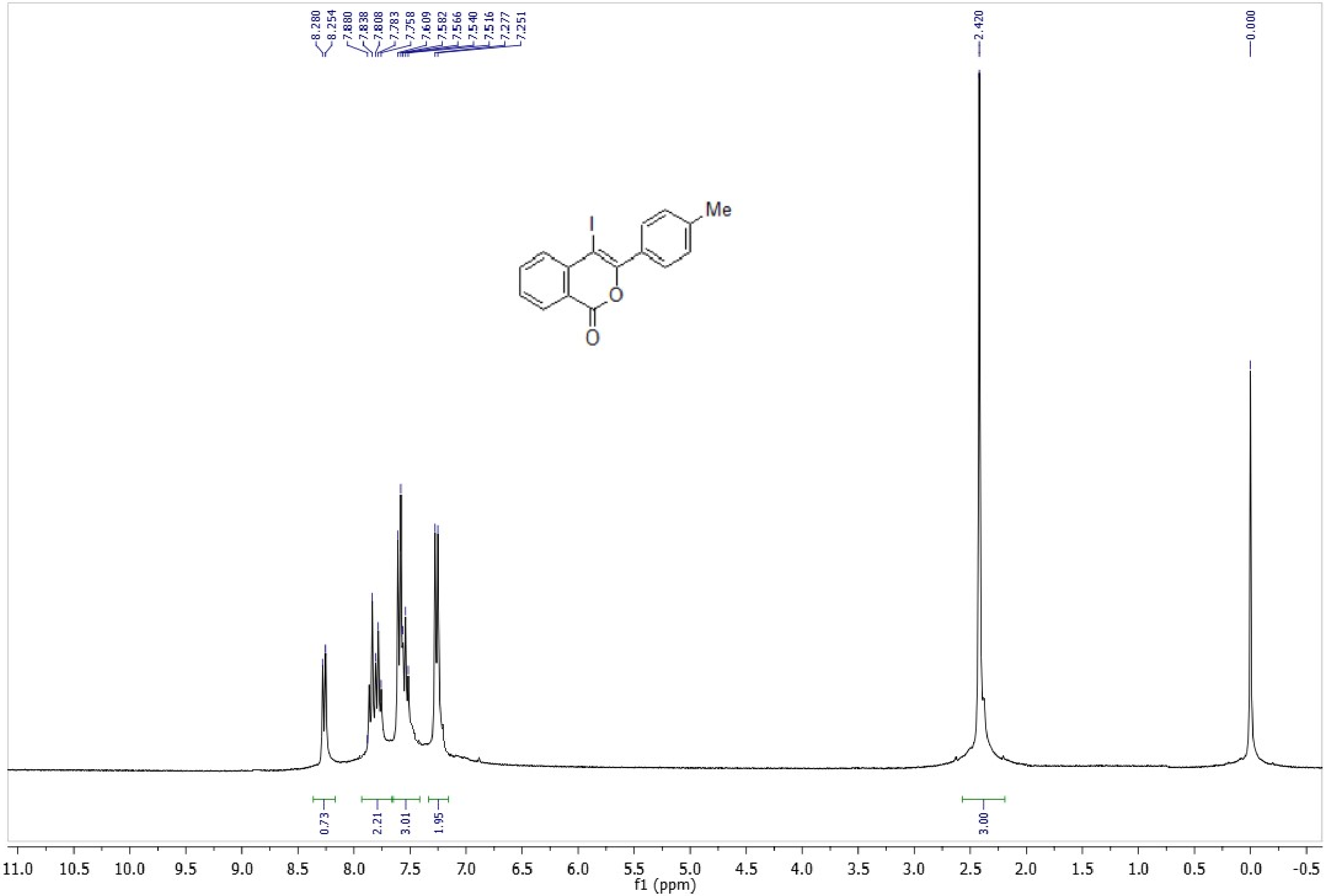


^{13}C NMR(CDCl$_3$)

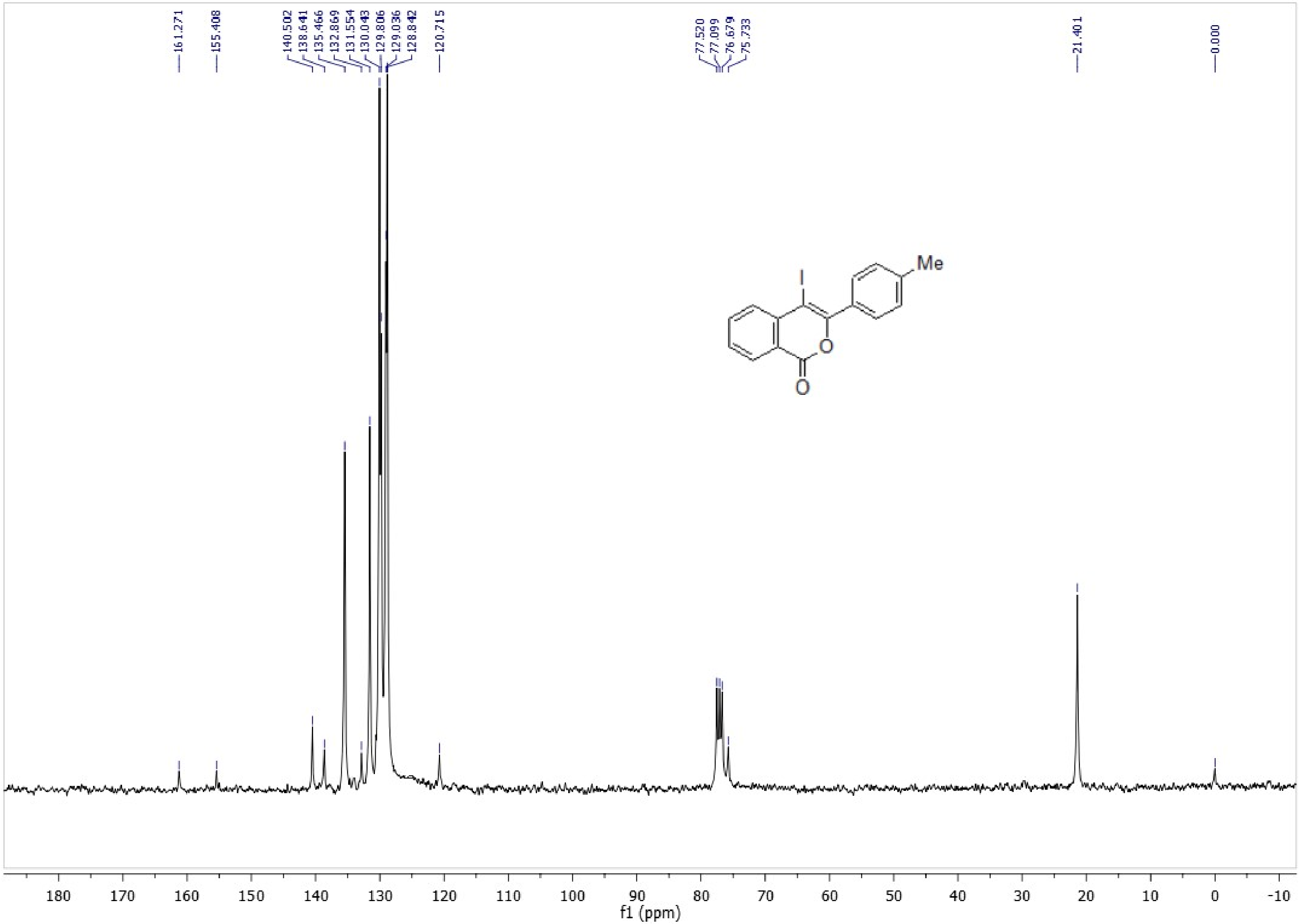


4-Iodo-3-*p*-tolylisochromen-1-one (**3h**)

^{1}H NMR($CDCl_3$)

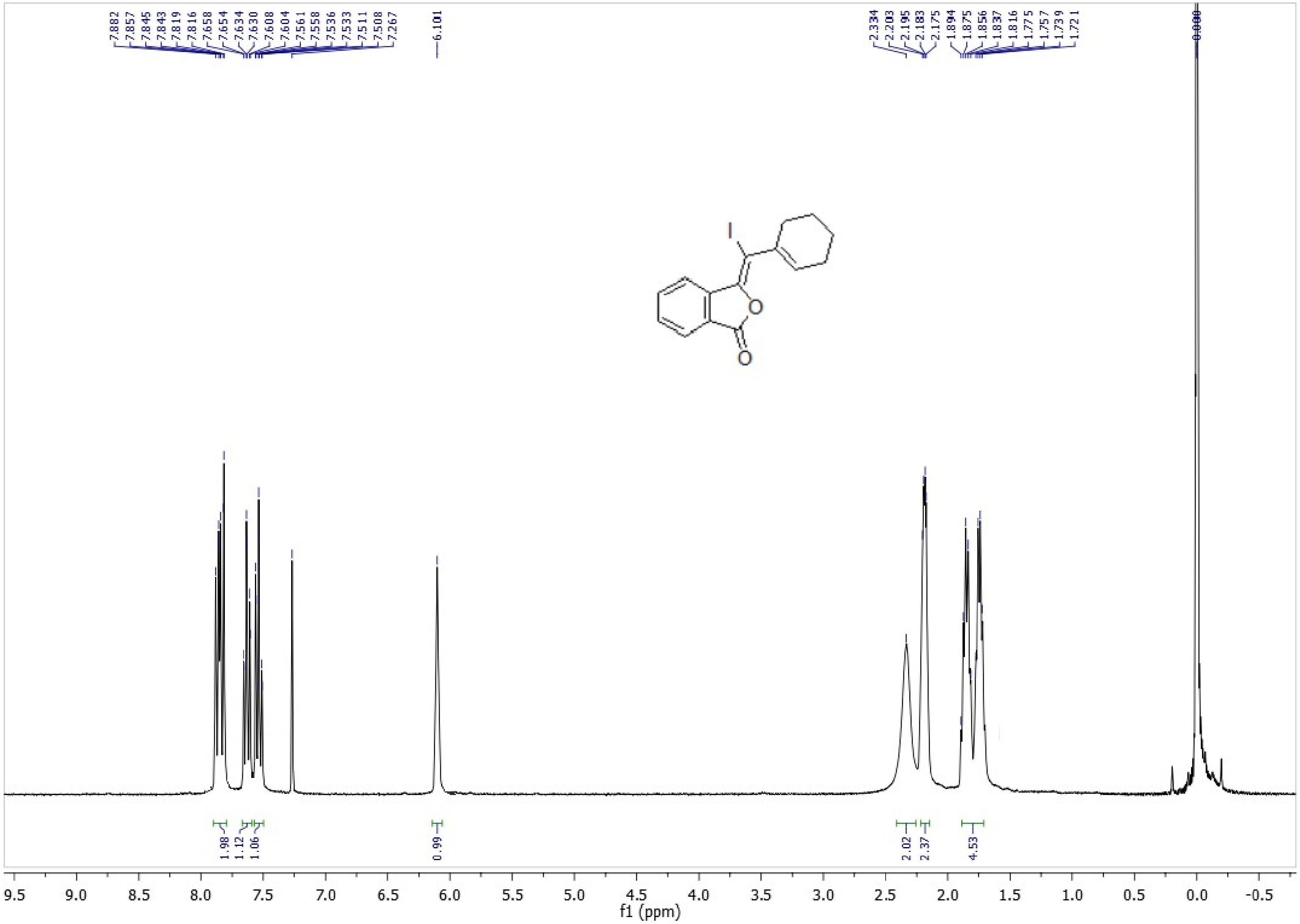


^{13}C NMR(CDCl$_3$)

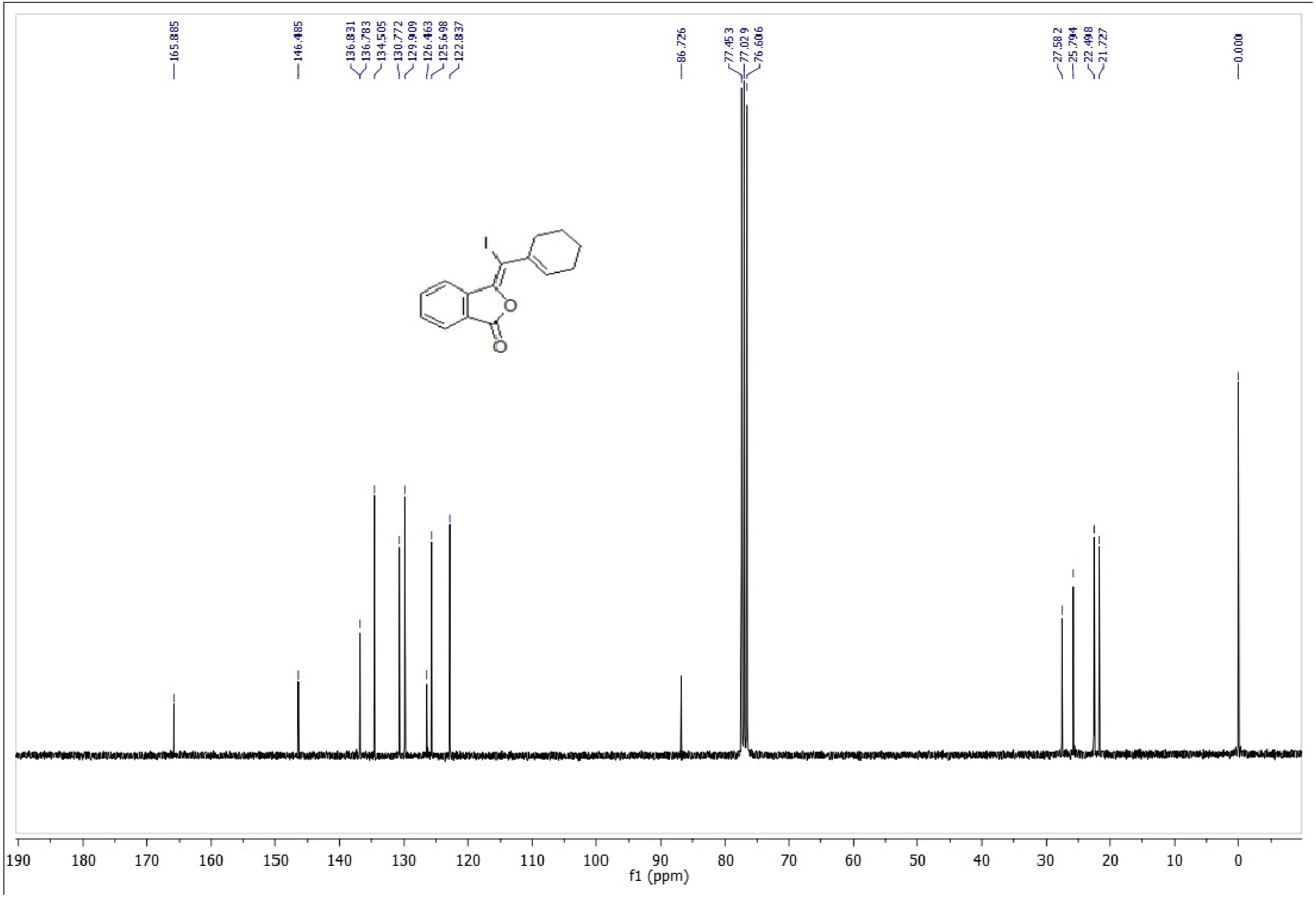


(*E*)-3-(Cyclohex-1-enyliodomethyene)-3H-isobenzofuran-1-one (2i)

^{1}H NMR(CDCl$_3$)

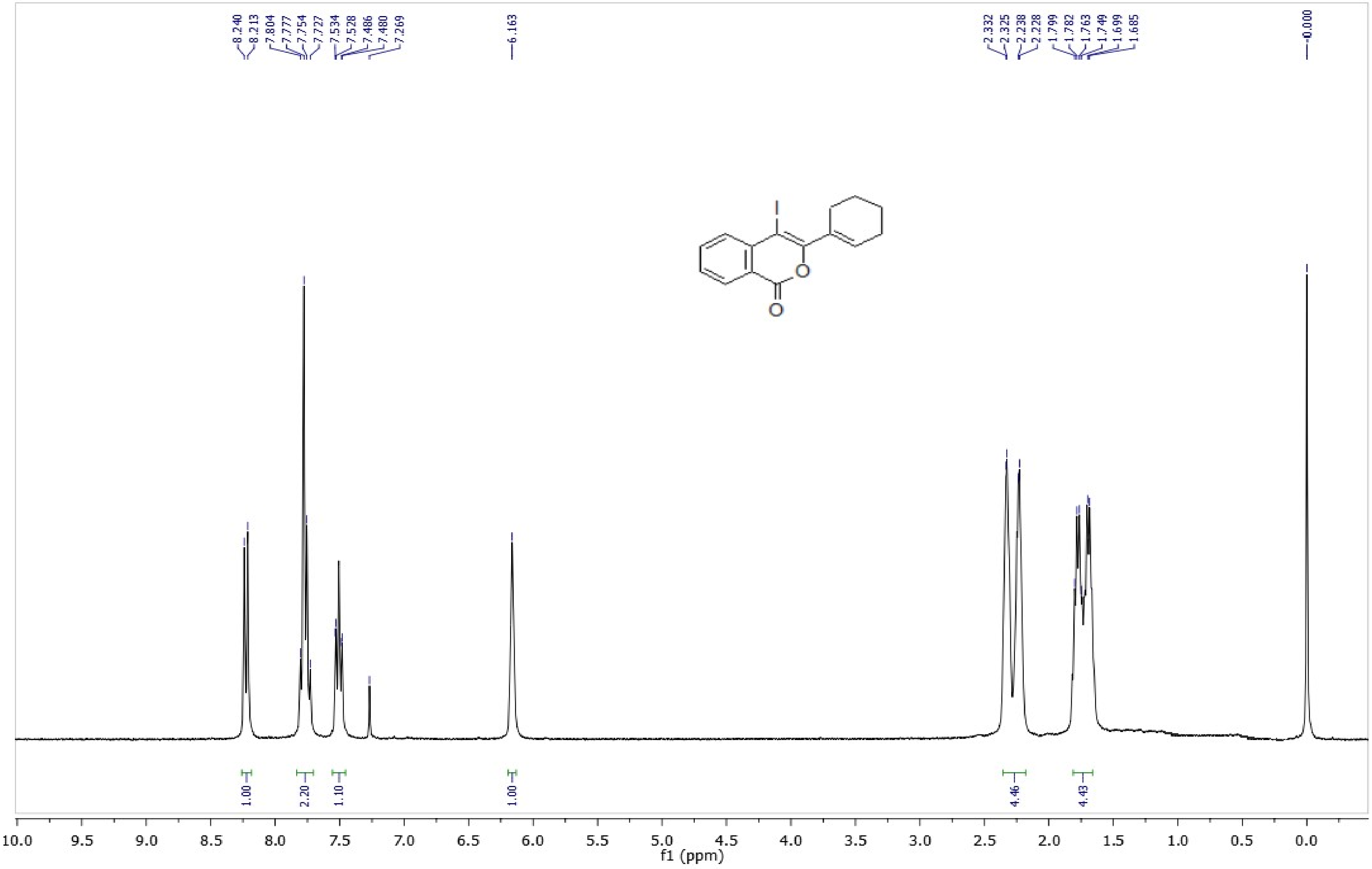


^{13}C NMR($CDCl_3$)

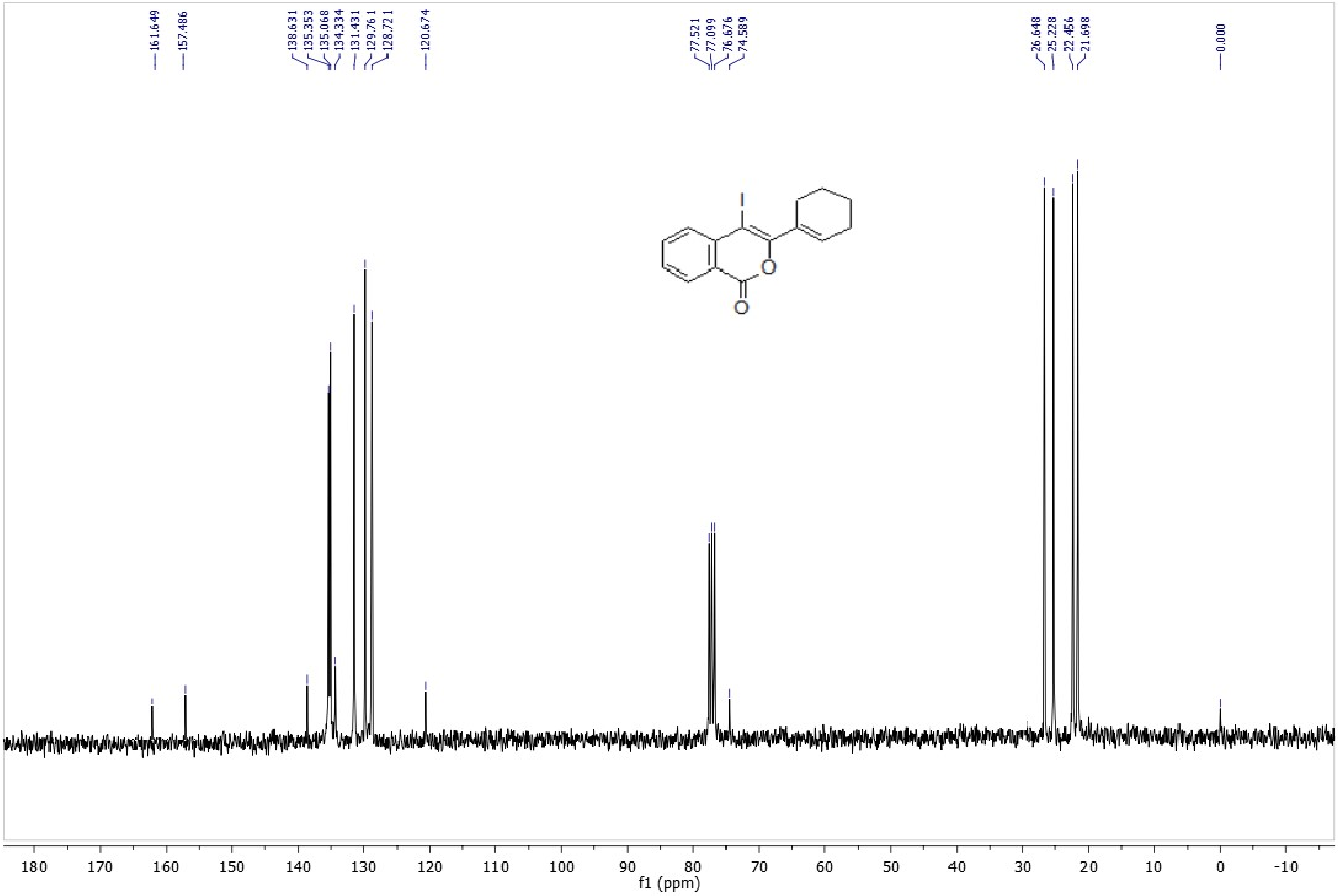


3-Cyclohex-1-enyl-4-iodoisochromen-1-one (**3i**)

^{1}H NMR(CDCl$_3$)

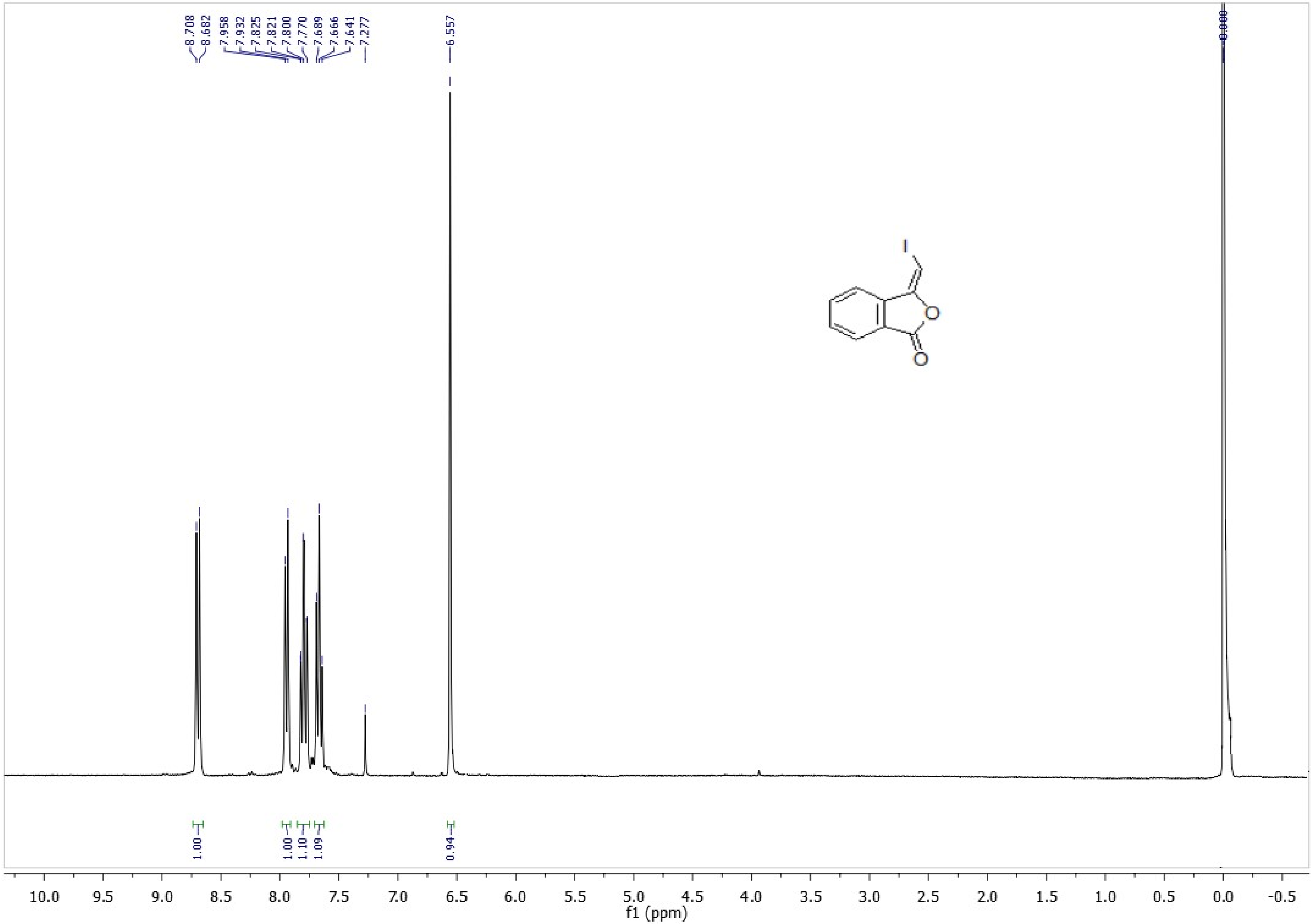


^{13}C NMR(CDCl$_3$)

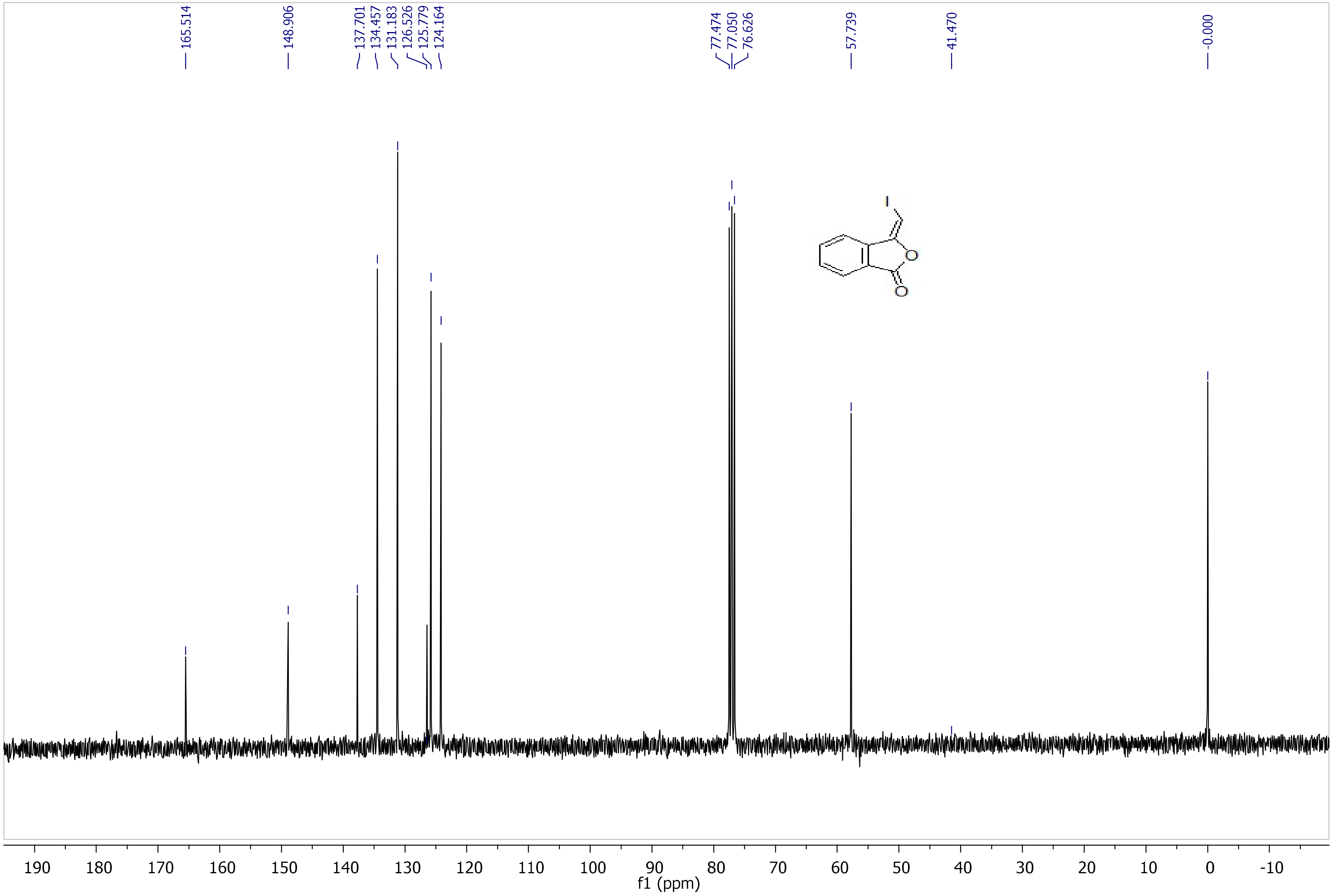


(E)-3-Iodomethylene-3H-isobenzofuran-1-one (2j)

^{1}H NMR(CDCl$_3$)



^{13}C NMR(CDCl$_3$)



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